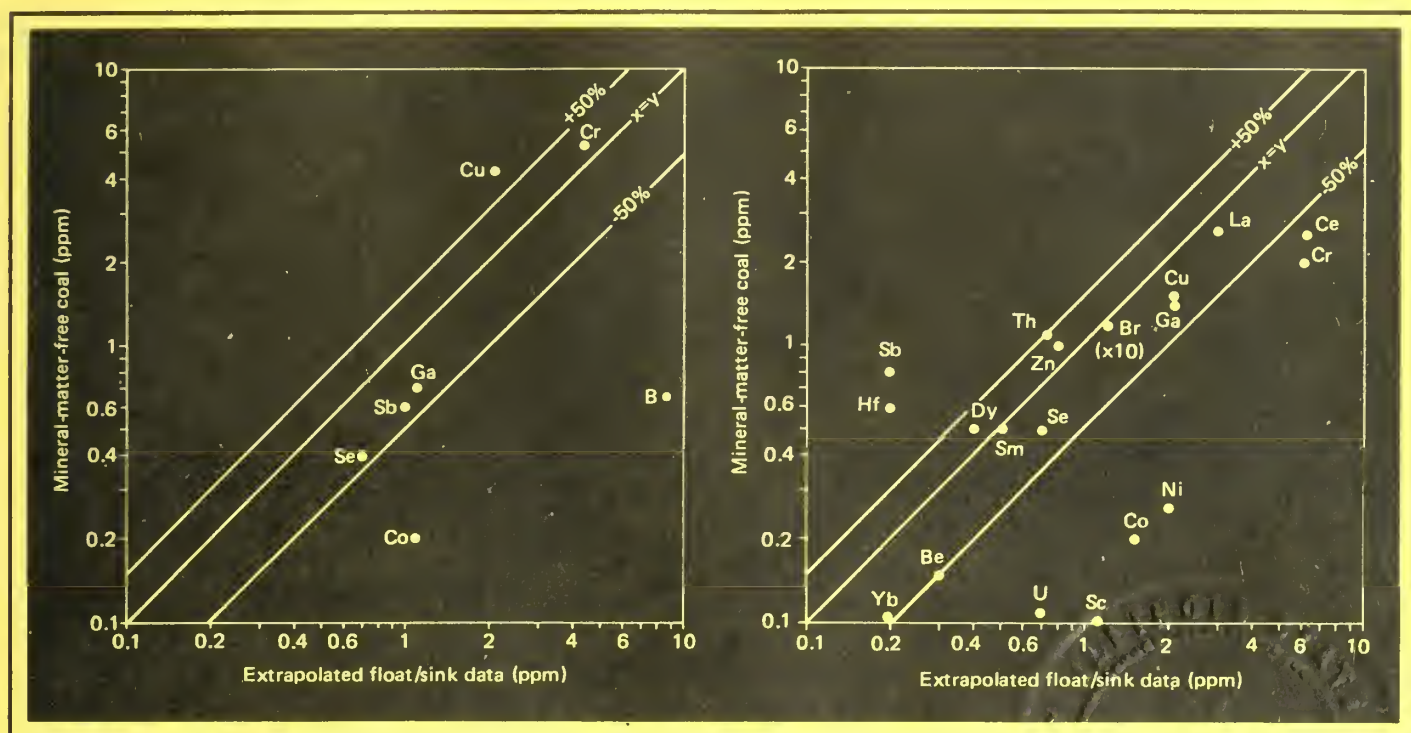


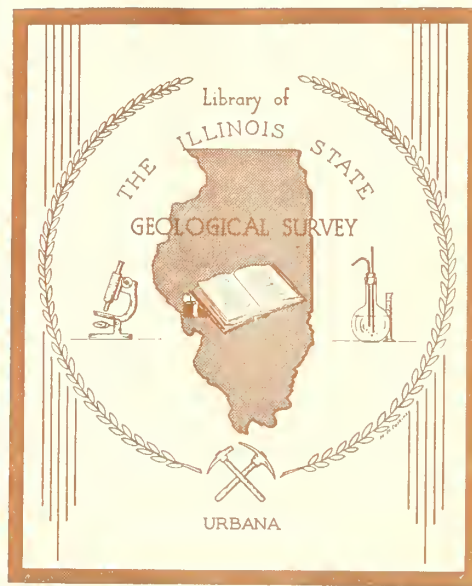
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Geol Survey

Abundance of Trace and Minor Elements in Organic and Mineral Fractions of Coal

J.K. Kuhn, F.L. Fiene, R.A. Cahill, H.J. Gluskoter, and N.F. Shimp





Cover figure: Comparisons of concentrations of organically associated elements independently derived from mineral-matter-free (acid-treated) coal and float/sink gravity fractions of coal. (Left) Illinois No. 6 seam; (Right) Pittsburgh No. 8 seam.

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Abundance of Trace and Minor Elements in Organic and Mineral Fractions of Coal

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ABSTRACT

New data on the abundance and mode of occurrence of trace and minor elements in coal are presented in this report. A summary of related studies previously conducted at the Illinois State Geological Survey is also included.

Twenty-seven coals, fifteen from Illinois, three from West Virginia, three from Alabama, two from Montana, and one each from Pennsylvania, Arizona, North Dakota, and Wyoming, were selected for study in the new phases of this work. Each coal sample underwent acid treatment, and selected coals underwent float/sink and ion exchange treatments. From these treated samples, coal fractions were obtained and analyzed by various methods.

An enriched organic-matter fraction, virtually free of mineral matter, was prepared by extracting coal under prescribed conditions with dilute nitric, hydrofluoric, and hydrochloric acids. Excluding organic sulfur, the resulting demineralized product contained no detectable coal minerals and only 250 to 600 ppm of ash-forming elements. These elements, and certain of the more volatile ones, are securely bound within the organic coal matrix; consequently, they were termed organically associated.

The concept of an organic affinity index was used to measure the tendency of an element to associate with the organic matter in coal. Of the elements studied, B, Be, Br, Ge, and Sb were consistently classified organic; sulfide-forming elements, Zn, As, Cd, and Fe, were classified inorganic; and others, such as Al, Ca, Ga, Ni, P, Si, and Ti, were intermediate or variable in their association. Generally, concentrations of organically associated trace elements were low, the lowest of which occurred in western coals. Conversely, western coals contained the greatest number of elements associated with organic matter.

Three general observations were made: (1) the total concentration of an element in coal is not indicative of its concentration in the organic phase; (2) because concentrations vary widely, accurate appraisals of trace and minor element associations by the methods used require that each coal be evaluated separately; and (3) the highest concentrations of trace and minor elements in coal are associated with mineral matter.

The validity (accuracy) of results for elements associated with the organic phase of coal was supported by the unexpectedly good agreement between two independent sets of values. One set was obtained by direct analysis of the acid-treated coal; a second set of values was derived from extrapolation of adjusted washability curves to zero percent recovery. Initially, these curves were used for calculating the organic affinity index. The values obtained by extrapolation represent the theoretical concentration of an element in a coal when no mineral matter is present. Further evidence for valid results stems from the fact that acid treatment did not alter organic sulfur concentrations and, therefore, probably did not significantly alter the coal structure itself.

In some coals, variations existed between values obtained from the two independent procedures for estimating organically associated elements; however, these differences can be explained by exchangeable ions on coal surfaces and by the solubility of some minerals. Acid treatment of coal removed exchangeable and soluble ions, but float/sink procedures did not. Failure to remove these elements from the coal organic fraction inflated the organic affinity index. Differences were apparent for Na, Ca, Mg, Ba, and B in western low-rank coals where, for example, more than 70 percent of the total Ca and Mg occurred in soluble or exchangeable forms. When allowance for such differences is made, the values for organically associated elements obtained by the two methods are in good agreement; they are thought to be reasonable estimates of concentrations in coal organic matter.

Despite evidence that many elements exhibit some degree of organic association, most of the trace and minor elements in these coals were in a mineral form. Thus many elements could be significantly reduced by physical cleaning procedures. The degree of reduction depends on the mineral, its size, and its distribution. Detailed mineralogic and microscopic analyses of low-temperature ash residues were made of gravity separations from nine of the coals. The same mineral data were obtained for 26 of the 27 whole coals studied. Western coals had distinctly

different mineral suites than Illinois and eastern coals; kaolinite predominated over other clay minerals, and significant amounts of bassanite were formed during the low temperature ashing process. Western coals also contained minor quantities of calcite, quartz, and pyrite. General associations were compiled for trace elements with minerals.

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SECTION I

INTRODUCTION

Although coal is the most abundant fossil fuel resource in the United States, environmental restraints are preventing its optimum use. A primary cause of these restraints is the occurrence of accessory elements and minerals in association with the coal. Their abundance and especially their type of association or combination can have a significant effect on the ease with which these elements and minerals are removed before the coal is used. For example, organic sulfur, which is not removed from coal by physical cleaning methods, appears in process streams and effluents as an undesirable constituent and must be removed later. Adverse characteristics may be identified in other organically associated elements in coal. An element's form does affect the extent to which it can be removed or recovered.

Little direct evidence for the kinds and concentrations of elements in the organic fractions of coal is available. That some elements in coal have either a high organic or inorganic affinity was considered more than 40 years ago by V. M. Goldschmidt, who pioneered modern investigations of trace elements in coals. He identified trace elements in inorganic (mineral) combination in coals. He also postulated the occurrence of metal-organic complexes in coal; the observed concentrations of vanadium, molybdenum, and nickel were attributed to the presence of such complexes (Goldschmidt, 1935).

Nicholls (1968) plotted the concentration of an element in coal or in coal ash against the ash content of the coal. Diagrams depicting a number of such points for a single coal seam, or for a group of coal seams in a single geographic area, were interpreted for degree of inorganic or organic affinity of the element. Nicholls described elements as (1) associated with the organic fraction, (2) generally associated with the inorganic fraction; and (3) elements that could be associated with either or both fractions.

Horton and Aubrey (1950) handpicked pure vitrain samples from coals and separated the samples into five different specific gravity fractions. They then analyzed these fractions for minor elements. For the three vitrains that were studied, they concluded that beryllium, germanium, vanadium, titanium, and boron were contributed almost entirely by the inherent (organically combined) mineral matter and that manganese, phosphorus, and tin were associated with the adventitious (inorganically combined) mineral matter.

Results of investigations of the organic-inorganic affinities of trace elements in coals were published by Zubovic, Stadnichenko, and Sheffey (1960, 1961, 1964). In more recent articles Zubovic (1966, 1976) listed 15 elements

in decreasing order of percentage of organic affinity. He suggested also (1976, p. 50) that the metals having high organic affinities in coal are present as chelates.

Ruch, Gluskoter, and Shimp (1974) and Gluskoter (1975) published tables of organic affinities for 21 elements determined on four samples of Illinois coals, which had been separated into specific gravity fractions in the laboratory. They listed the elements in decreasing order of organic affinity, but numerical values were not given for the index. Since these results were published, Gluskoter et al. (1977) and Kuhn et al. (1978) reported washability data for up to 53 elements and 10 coal parameters from seven additional coals. They calculated an index of organic affinity from washability curves for the elements determined in the washed coals. Gluskoter et al. (1977) presented tables that listed the organic affinity index values for nine coals and ranked the elements as "organic," "intermediate-organic," "intermediate inorganic," and "inorganic." Each coal analyzed was ranked separately because an element that is "organic" in a sub-bituminous coal from Wyoming may be "inorganic" in an Appalachian coal. A study recently completed at the Illinois State Geological Survey and briefly reported by Kuhn et al. (1978) used chemical demineralization of coal as a totally independent approach. The study obtained results that were applied to the determination of organic affinities. Fiene, Kuhn, and Gluskoter (1978) reported on the mineral phases found in the same coal samples as those studied by Gluskoter et al. (1977), Kuhn et al. (1978), and Kuhn, Fiene, and Harvey (1978). The study determined minerals in both the low temperature ashes of the coals and their specific gravity fractions. Data from these studies are summarized in this report and are combined with results of our new research to provide a single source of information on the occurrence of organically associated trace elements in coal.

The scope of this work includes nine coals, separated into specific gravity fractions, from the eastern, central, and western portions of the United States. To gain a wider distribution of sample types, another 18 coals were also subjected to chemical demineralization. Ion exchange determinations were performed on seven coals. Chemical and mineralogical analyses were made on all of these materials; however, in an effort to remain as concise as possible, only the values regarded as pertinent to conclusions for this study are presented.

SECTION II

CONCLUSIONS AND RECOMMENDATIONS

The chemical form of an element influences its behavior during coal processing and pyrolysis. In this study, procedures for determining the forms in which minor and trace elements occur in coal were investigated.

Two methods—chemical and physical—were used to prepare highly enriched organic fractions of coal. Comparison of results from analyses of these fractions enabled reasonable estimates to be made of the concentrations of up to 45 minor and trace elements associated with coal organic matter. These values, all of which were low in comparison to total amounts, are believed to represent the theoretical lower limit attainable for an element in cleaned coal. The concept of an organic affinity index to measure the tendency of an element to remain with the coal organic matrix is reviewed and expanded.

Forms of elements other than organically associated ones were also investigated; significant concentrations of exchangeable and acid soluble elements, e.g., Ca and Mg, are more abundant in western coals than in eastern or Illinois Basin coals. Unless these elements were first removed or taken into account, estimates of the organically associated elements were inflated for the low rank coals. In addition, the western coals contained different mineral suites. General mineral associations were compiled for trace and minor elements.

Chemical form is believed to be only one of the factors controlling element behavior. Preliminary evidence from our current research indicates that the occurrence and distribution of certain elements in the products of pyrolysis is also influenced by the conditions under which coal is pyrolyzed. Thus, an element with a high organic affinity—or two different elements with equally high affinities—may report to very different coal fractions when pyrolyzed under different conditions. A knowledge of process conditions and organic affinities needs to be considered if accurate estimates are to be made of distributions of elements in process streams.

Organic affinity indexes, if made sufficiently accurate for a range of coals, could be used in conjunction with total concentrations for determining, in addition to sulfur, the chemical forms of many elements, for estimating the theoretical percentage of an element that can be removed by coal cleaning, and for predicting material balances in the coal products and wastes. Before this is feasible, however, additional evidence for the validity of the organic affinity concept is needed.

SECTION III

METHODS

SAMPLING

Twenty-five of the 27 coals used in this study were face-channel or composite face-channel samples collected in coal mines by Illinois State Geological Survey personnel. The two exceptions were obtained from a Federal agency. The 25 samples were hand cut and represent the full face of the coal seam excluding mineral bands, nodules, and partings greater than 1 cm thick, following an established procedure described by Holmes (1911). All were air dried and riffled according to standard procedures of the American Society for Testing and Materials (1978a). Representative portions of the raw coal were stage ground to -60 mesh (250 μm) for chemical analysis and low-temperature ashing and to -100 mesh (149 μm) in a Pitchford uniform-particle-size grinder for trace element determinations. Subsamples used for acid demineralization were comminuted to less than -325 (44 μm) mesh in a ball mill. Table 1 lists the whole coal samples used in these projects; each material is assigned an analysis number ("C" number), which is used for identification throughout this report.

ANALYTICAL

Analytical methods used for the analysis of samples are given in table 2. Details of these methods were reported by Gluskoter et al. (1977), except for the energy dispersive X-ray fluorescence method, which is contained in Ruch et al. (1979). Although the methods are the same, the elements determined by each method are not entirely comparable with those described by Gluskoter et al. Methods requiring ashing procedures, e.g., atomic absorption and optical emission, could not be used because of the extremely low level of ash in the acid demineralized coal (MMF). Except in the case of Be, attempts to analyze whole coal samples by optical emission failed because the necessary sensitivity could not be achieved.

In most cases, for any particular element, a single method was used to analyze an entire set of samples. However, for the nine float/sink sets, different methods were used for some elements and could bias results, especially at very low concentrations.

This study uses three different approaches to the investigation of the mode of occurrence of trace elements in coals. The first approach is based on differences in specific gravity or "coal washing" and seldom, if ever, results in a complete separation of mineral matter from the coal. Rather, a fractionation results in which the parts are enriched in either mineral or organic matter. A second approach, which is basically a chemical demineralization of the coal, was used in an attempt to achieve a more complete separation of the organic and mineral fractions of coal than is possible by gravity separations. Extraction of exchangeable ions with a neutral, buffered solution was the third approach used.

TABLE 1. Whole coal selections

Number	Coal seam	State
C-18126 †	Herrin (No. 6)	Illinois
C-16543	Herrin (No. 6)	Illinois
C-16993	Herrin (No. 6)	Illinois
C-17001 *	Davis	Illinois
C-18304	De Koven	Illinois
C-18560 *	Herrin (No. 6)	Illinois
C-18704	Herrin (No. 6)	Illinois
C-18816	Mammoth	Montana
C-18820 *	Pocahontas (No. 4)	West Virginia
C-18841 *†	Pittsburgh (No. 8)	West Virginia
C-18848 *†	Blue Creek	Alabama
C-18857	Herrin (No. 6)	Illinois
C-19000 *†	Black Mesa Field	Arizona
C-18571	Herrin (No. 6)	Illinois
C-18844	Pittsburgh (No. 8)	Pennsylvania
C-19824 *†	Pittsburgh (No. 8)	West Virginia
C-19854 *†	Rosebud	Montana
C-18824	Johnson	Alabama
C-18440 †	Noonan	North Dakota
C-18748	Abbott Fm.	Illinois
C-18320	Herrin (No. 6)	Illinois
C-18368	Herrin (No. 6)	Illinois
C-18445	Rosebud	Montana
C-18457	Hanna 24	Wyoming
C-14684	Herrin (No. 6)	Illinois
C-15999	Herrin (No. 6)	Illinois
C-16173 *	Herrin (No. 6)	Illinois

*Samples for which gravity separations were made.

†Samples for which ion exchange determinations were made.

CHEMICAL DEMINERALIZATION

The method used to chemically remove minerals from the organic fraction of the coal is a variation of the procedure for the determination of forms of sulfur in coal (American Society for Testing and Materials, 1978b), in which HCl and HNO₃ are used under prescribed conditions to extract sulfate and pyritic sulfur. In this study, HF is also used to dissolve the silicate minerals in a manner similar to that described by Bishop and Ward (1958) and by the International Organization for Standardization (1974).

The coal was first floated at 1.40 specific gravity in perchloroethylene and naphtha to reduce the mineral phases, especially pyrite. Dissolution of

TABLE 2. Analytical methods used in this study

Instrumental neutron activation:

Fe, Na, K, Mn, Sc, Cr, Co, Ni, Zn, Ga, As, Se, Ba, Rb, Sr, Mo, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Dy, Yb, Lu, Hf, Ta, W, Th, U, I,* Ag,* Au*

X-ray fluorescence—Wavelength dispersive:

Si, Al, Fe, Ca, Mg, Ti, P, Mn, V, Cu, Pb

Direct reading optical emission:

Be

Prompt gamma ray/neutron activation:[†]

B

X-ray fluorescence—Energy dispersive:

Ba, Cd, I,* In,* Sn,* Te*

*Elements not reported. Most values were below detection limits.

[†]Work performed by E. S. Gladney, Los Alamos Scientific Laboratories, NM.

the minerals in the demineralizing solutions could add to the concentration of elements associated with the organic matter, and it was deemed desirable to reduce elemental concentrations in the solutions as much as possible. We have assumed, as others have in the past, that the coal organic material is unaltered by this process, although little evidence is available to support or disprove the assumption.

The float fraction was then comminuted to less than -325 (44 μ m) mesh, and 10-gram samples were placed in a flask containing a cold finger condenser and 50 mL of 10 percent HNO_3 and refluxed for 1, 2, or 3 hours. The materials were quantitatively removed from the flask and were filtered, washed, and dried at room temperature overnight. The samples were then placed in polyethylene flasks, covered, and allowed to digest in 49 percent HF at 70°C for periods of 1, 2, or 3 hours. The material was again quantitatively removed from the flasks, filtered in plastic funnels, washed, and dried. Finally the materials were placed in a flask and, utilizing a cold finger condenser, were refluxed for 1 hour with 25 percent HCl at approximately 100°C. After refluxing, the materials were quantitatively removed from the flasks, filtered, washed, and dried. (Yields of coal organic material from this procedure were not measured.) The samples were subsequently analyzed by the analytical methods in table 2.

A number of coals were processed by this procedure to ascertain the conditions for use with subsequent samples. An example of the results is shown in table 3. It was concluded from these tests that no significant advantage was gained from refluxing the materials for 3 hours. Because the intent was to cause as little change in the nature of the coal as possible,

TABLE 3. Effect of physical and chemical treatments
on the concentrations of some elements
in a Herrin (No. 6) Coal sample

Element	Raw coal		1.40 float		1-hr treatment *		2-hr treatment *		3-hr treatment *	
	(%)	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)	(ppm)
Al	1.40		1.08			124		35		31
Si	3.20		2.15			250		41		42
Ca	.51		.094			33		25		23
K	.13		.11			1		1		1
Na	.04		.027			7		5		6
Cl	.05									
S	6.45		3.59		2.64		2.52		2.54	
Fe	2.60		.90			170		66		65
Ti	.06		.08			25		11		14
Organic S	2.55		2.66		2.64		2.52			
P		50		13		9.7		<1.0		<1.0
As		3.4		2.8		.1		.1		.1
Pb		<.1		<.1		<.1		<.1		<.1
Br		3.5		3.4		2.4		2.9		2.5
Cu		13		13		3.4		2.1		2.2
Ni		24		7.5		2.5		<1		1
Zn		43		20.5		8.8		4.4		4.0
V		36		28		6.1		3.5		3.3
Rb		23		10		<1		<1		<1
Cs		2.0		.7		<.1		<.01		<.01
Ba		54		42		21		3.6		2.8
Sr		28		10.3		1.8		1.3		1.1
Sc		4.1		2.8		.9		.5		.5
Cr		21		16.8		8.8		6.2		6.1
Co		5.5		3.7		.4		.4		.4
Ga		2.4		2.8		.9		.6		.6
Se		4.3		1.4		.2		.3		.2
Sb		.4		.2		.1		.1		.1
Hf		1.1		.5		.1		.1		.1
W		.5		.3		.1				
La		6.1		3.4		.9		.6		.6
Ce		25		7.3		1.8		1.5		1.5
Sn		.8		.8		.4		.35		.3
Eu		.2		.2		.1		.1		.1
Dy		1.2		.6		.5		.4		.5
Lu		<.02						.02		
Yb		.8		.5		.2		.20		.2
Tb		.4		.1		.1		.09		.1
Th		3.6		1.9		.9		.88		.9
U		1.9		.5		.2		.09		.1
Mo		18		3.5		.5		.44		.4
Hg		.23		.1						
Mn		60		10.3		.4		.3		.2

NOTE: All values normalized to raw coal.

*Includes HNO₃ and HF but not HCl.

the 2-hour refluxing and digestion procedure was adopted. This procedure was selected although it is recognized that in some instances, such as, in peat or materials with high silicon content, total elimination of the mineral-matter content in coal may not result.

Further tests were made to determine the extent to which the coals were demineralized. The acid-extracted coal product was subjected to low temperature ashing, a process which destroys organic matter but leaves minerals relatively unaltered. Ash percentages ranged from 0.32 percent to 1.69 percent, and x-ray diffraction analysis of the residues failed to detect any of the minerals originally present in the whole coals. Only traces of chloride and fluoride were detected, and these probably originated in the acid treatment. The absence of detectable minerals from the whole coal supported the belief that the samples were now virtually free of mineral matter.

It is known that HNO_3 oxidizes organic materials; consequently, a second procedure was investigated using the reducing agent lithium aluminum hydride (LAH), instead of HNO_3 , for removal of pyrite and other sulfides. Previous work has shown the procedure to be an acceptable and, in some instances, a preferable substitute for the HNO_3 digestion (Lawlor, Fester, and Robinson, 1963; Kuhn, Kohlenberger, and Shimp, 1973). Table 4 compares the results of the two procedures, and although a few minor differences exist (e.g., Fe and Mn), the two sets of values compare quite favorably. While the procedure using LAH yields approximately the same values as the nitric acid method, the latter was selected because it requires less time and is less hazardous.

Another aspect which was considered during development of the demineralization procedure is the common occurrence of minute, widely disseminated mineral grains, which may be occluded within organic coal particles. For this reason, the coals extracted for this study were pulverized to a very fine size (approximately -325 mesh) after the 1.40 gravity separation was performed. Because some mineral particles occur as submicron crystallites, the data determined may well represent the limits to which the coal can be cleaned by practical methods. The terms "organic association" and "organic affinity" rather than "organic combination" are, therefore, preferred for elemental concentrations in "mineral-matter-free" coal.

PHYSICAL DEMINERALIZATION

About half of the coals produced in the United States are "washed" or "cleaned" prior to delivery to the consumer. Cleaning involves reducing the content of ash and sulfur of the coal by removing a portion of the mineral matter associated with the coal. Because specific gravities of the minerals in coal are from two to four times greater than that of the organics (macerals) in the coal, conventional coal-cleaning techniques involve specific gravity separations.

Nine coal samples were separated into specific gravity fractions and were analyzed for major, minor, and trace elements. Gravity separations were made on a 3/8-inch by 28-mesh fraction, obtained by stage grinding and screening the coal. The sized coal was separated into five or six specific gravity fractions ranging from 1.28 float to 1.60 sink in mixtures of perchloroethylene and naphtha. Chlorine values in the washed coals are unreliable because relatively large and variable amounts of this element may have

TABLE 4. LAH extraction versus HNO₃ extraction

Element	IL No. 6 C-14684		Subbituminous C-18457		IL No. 6 C-15999		IL No. 6 C-18560	
	LAH (ppm)	HNO ₃ (ppm)	LAH (ppm)	HNO ₃ (ppm)	LAH (ppm)	HNO ₃ (ppm)	LAH (ppm)	HNO ₃ (ppm)
Al	45	82	115	78	282	77	400	35
Si	65	98	83	69	122	81	95	41
Ca	10	19	21	16	74	41	80	25
K	<10	<10	<10	<10	<2	<1.1	<5	1
Na	<4	1	21	11	4	6	18	6
Fe	700	93	800	56	900	64	700	66
Ti	58	58	43	30	60	56	100	90
P	2	5	<1	<1	7	5	6	<1
V	4	6	2.0	2.1	4	7	5	3.5
Cu	2.2	2.2	2.1	2.4	1.6	1.4	2	2.1
Rb	<1.0	<1.0	<.1	1.2	<1	<1	<1	<1
Cs	.1			.06	<.1	<.1	<.1	.1
Ba	<10	4.2	<10	2.6	<10	4.6	<10	.2
Sr	2.9	3.5	6.2	3.7	8.1	5.5	7.9	1.5
Br	15	9.2	1.0	.1	7	6	4.8	3.3
Sc	.1	.6	.2	.4	1.3	1	2.2	.6
Cr	3.3	4.6	4.1	1.2	<1	7.4	8.4	6.8
Mn	1.3	.3	6.0	.2	5.0	.3	4.6	.3
Co	.5	.9	.1	.2	1.0	.4	2.4	.4
Ni	<10	3.6	<1	<5	<5	4.7	<1	<1
Zn	<1	<1	<1	<1	<1	<1	<1	<1
Ga	.5	.5	.3	.4	1.5	.8	1.3	.7
As	3.7	.2	.7	.5	4.0	<.1	1.3	.1
Se	.6	.3	.4	.3	1.0	.3	1.2	.3
Sb	.2	.5	.2	.2	.8	.5	<.1	.1
Hf	<.1	.2	<.1	.3	<.1	.1	<.1	.1
W	<.5	.1	<.1	.1	<.5	.1	<.5	<.5
La	1.5	.8	.6	1.0	2.0	.6	1.3	.7
Ce	1.6	.4	1.2	1.2	1.1	1.3	1.5	1.7
Sm	.2	.2	.1	.1	.5	.22	.7	.4
Eu					.1	.1	.1	.1
Dy	.2	.2	.2	.2	.6	.5	.9	.5
Lu	<.1	<.1	<.1		<.1	<.1	<.1	
Yb	<.1	.2	<.1	.1	<.2	.2	.4	.2
Tb	<.1		<.1		.4	<.1	.8	.1
Th	.3	.6	.2	.7	1.2	.6	3.7	1.0
U	<.1	.1	<.3	.1	.2	.3	<.1	.1
Mo	<1	.4	<.5	.4	1.3	.6	.6	.5

been absorbed by the coals from the washing media. Therefore, these determinations have been deleted from the results.

EXCHANGEABLE IONS

Weakly bound (exchangeable) elements and soluble minerals were extracted from seven whole coals with ammonium acetate. Some minerals such as calcite, if present, were dissolved and extracted with the exchangeable ions; no attempt was made to distinguish between the two. For convenience, ions extracted by this process are termed exchangeable.

Coals used for the exchangeable ion studies were reduced to -325 mesh, and 10 grams were placed in a 300 mL polyethylene flask. Fifty mL of ammonium acetate (1N) were added to the flask, and the mixture, at an approximate temperature of 70°C, was then stirred for 20 hours. At the end of the exchange/dissolution period, the material was vacuum filtered while being flushed with sufficient ammonium acetate solution to bring the volume up to 450 mL. A final flush with 50 mL of ethyl alcohol was performed, and the sample was then vacuum dried. Elemental determinations were made on the residual coal material.

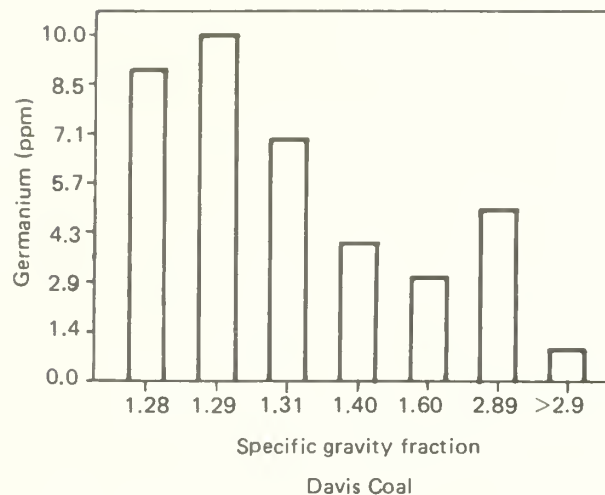
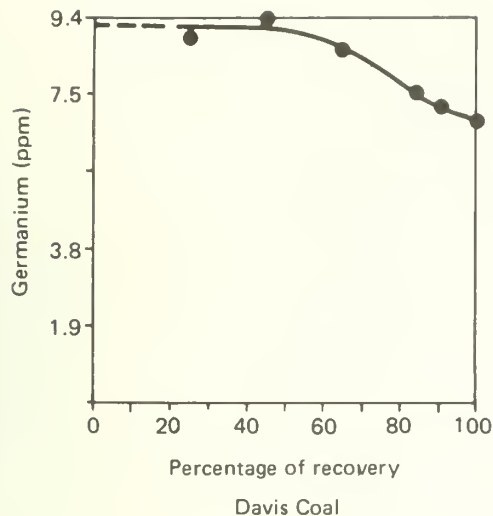
METHOD OF DISPLAYING WASHABILITY DATA

The float-sink or washability data can be displayed as washability curves and histograms. Data on the washability characteristics (sulfur and ash reduction) of many Illinois coals have been presented by Helfinstine et al. (1970) and by Helfinstine et al. (1971, 1974). Cavallaro et al. (1978) published washability curves for eight elements in ten coal samples collected from various coal-producing regions of the United States. The elements they determined were Cd, Cr, Cu, F, Hg, Mn, Ni, and Pb.

Figures 1 through 3 are examples of washability curves and histograms for three elements. The figures are presented in order of increasing tendencies of the elements to be concentrated in the heavier fractions (decreasing organic affinity). The washability curve is a type of cumulative curve from which the expected concentration of an element in a coal can be read at any given recovery rate, if one assumes that the separation was based on specific gravity differences. Therefore, the abscissa is "recovery of float coal in percent" and should be applicable to any specific gravity separation without regard to the medium in which it is done or the method used. The raw coal concentration of an element is read at the 100-percent recovery point; the concentration in the cleanest coals (most free of mineral matter) is read at the low recovery end of the curve (generally in the range 20 to 30 percent recovery).

Figure 1 shows the washability curve and the histogram for germanium in a sample from the Davis Coal Member. The negative slope of the curve indicates that germanium is concentrated in the clean coal fractions; this is also apparent from the histogram.

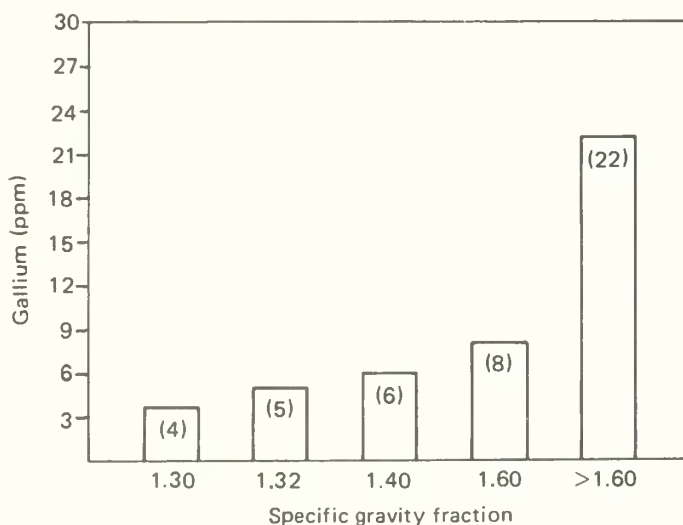
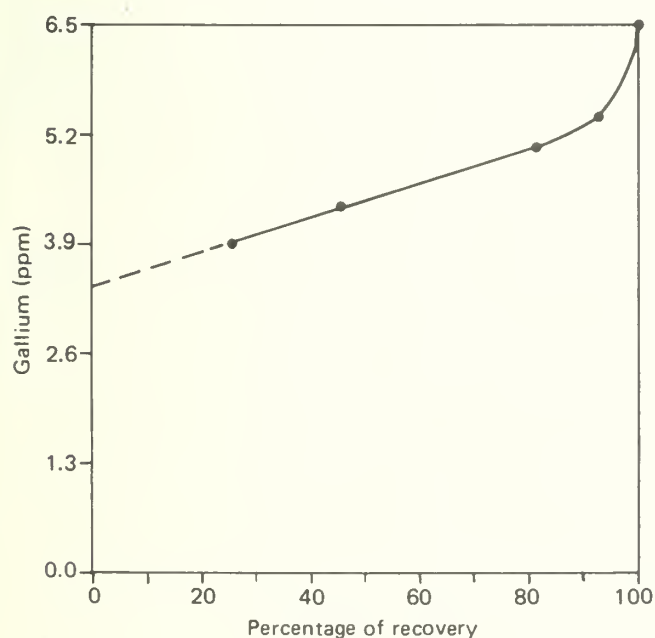
An element that is uniformly distributed in the various fractions of the washed coal will have a flat washability curve with a slope of zero. Washing such a coal will have no effect on the concentration of the element in the clean coal.



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Figure 1. Germanium in specific gravity fractions of a sample from the Davis Coal Member. Left: Washability curve. Right: Distribution of germanium in individual fractions.

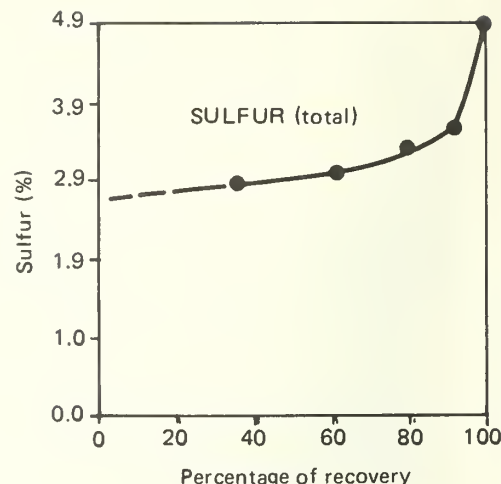
A positive slope of the washability curve shows that the element is concentrated in the inorganic (mineral matter) portion of the coal. The more strongly associated the element is with the inorganic fraction, the steeper is the slope of the curve. Washability data on Ga in a sample from the Blue Creek coal seam in Alabama give a washability curve having a positive slope. The curve does not approach the origin (fig. 2); rather, when extended, the curve intercepts the ordinate at approximately 3.5 ppm.



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Figure 2. Gallium in specific gravity fractions of a sample from the Blue Creek coal from Alabama. Left: Washability curve. Right: Distribution of gallium in individual fractions.

Sulfur is present in coals in both organic and inorganic combinations; standard analyses report the varieties of sulfur as sulfate sulfur, pyritic sulfur, and organic sulfur. In a sample from the Herrin (No. 6) Coal in Illinois, the washability curve for total sulfur shows the contribution from both organic and inorganic sulfur (fig. 3). The sulfur content decreases rather rapidly in the washed coal as that part that is concentrated in the heavier mineral-matter-rich portion (inorganic sulfur) is removed. Then the curve flattens because the lighter coal fractions also contain appreciable amounts of sulfur (organic sulfur).



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Figure 3. Washability curve of sulfur in specific gravity fractions of a sample from the Herrin (No. 6) Coal Member.

METHOD OF CALCULATING THE ORGANIC AFFINITY INDEX OF AN ELEMENT

Washability curves and histograms of washability data are effective means of depicting the mode of combination of elements in coal—they indicate whether the elements are associated with the organic or inorganic fractions of the coal. However, a much easier means of comparing results for different elements or coals was needed. Therefore, an attempt has been made to quantify the information presented on the curves by producing an "organic affinity" index.

The present report expands upon the work of Gluskoter et al. (1977) and clarifies both the rationale and the techniques used to obtain a value for an index of organic affinity. This is both appropriate and necessary because certain values obtained during the derivation of the index are germane to the verification of the elemental concentrations determined in demineralized coal. The decision to name the index "organic affinity" rather than "inorganic affinity" was arbitrary; one is the inverse of the other.

The shape of the washability curve is dependent upon the mode of occurrence of the element, the analyses of which are plotted on the curve. Therefore, the area under the curve is also dependent upon the mode of occurrence of the element. The value for the organic affinity index for a specific element is obtained by calculating the area beneath the washability curve. This calculation is done on a curve that has been drawn to a predetermined and constant scale (normalized) and on a curve that has been adjusted for that part of the mineral matter that is inseparable from the lightest coal fraction. An example of the calculations necessary to obtain the organic affinity index follows using the data for chromium in table 5. A normal washability curve can be constructed with cumulative concentration values generated from the following equation:

$$\text{CALPPM}(I) = \frac{[\text{CALPPM}(I-1) \cdot \text{SUMPCT}(I-1)] + [\text{RECPCT}(I) \cdot \text{ANLPPM}(I)]}{\text{SUMPCT}(I)}$$

where,

TABLE 5. Chromium in specific gravity fractions of a washed sample of Herrin (No. 6) Coal in Illinois (normal and adjusted cumulative concentrations)

Analyses number	Specific gravity fraction	Percentage of raw coal (RECPCT)	Chromium (ppm) (ANLPPM)	Low temperature ash (%)	Cumulative percentage of raw coal (SUMPCT)	Cumulative chromium (ppm) (CALPPM)	Adjusted chromium (ppm)	Cumulative adjusted chromium (ppm) (CALPPM)
C18123	1.25F	36.1	8.0	3.84	36.1	8.0	4.9	4.9
C18124	1.29FS	17.4	12		53.5	9.3	8.9	6.2
C18125	1.33FS	14.7	16		68.2	10.7	12.9	7.7
C18126	1.40FS	9.3	25		77.5	12.5	21.9	9.4
C18127	1.60FS	6.9	33		84.4	14.1	29.9	11.1
C18128	1.60S	15.6	71	88.4	100	23.0	67.9	19.9

CALPPM = the cumulative elemental concentration,

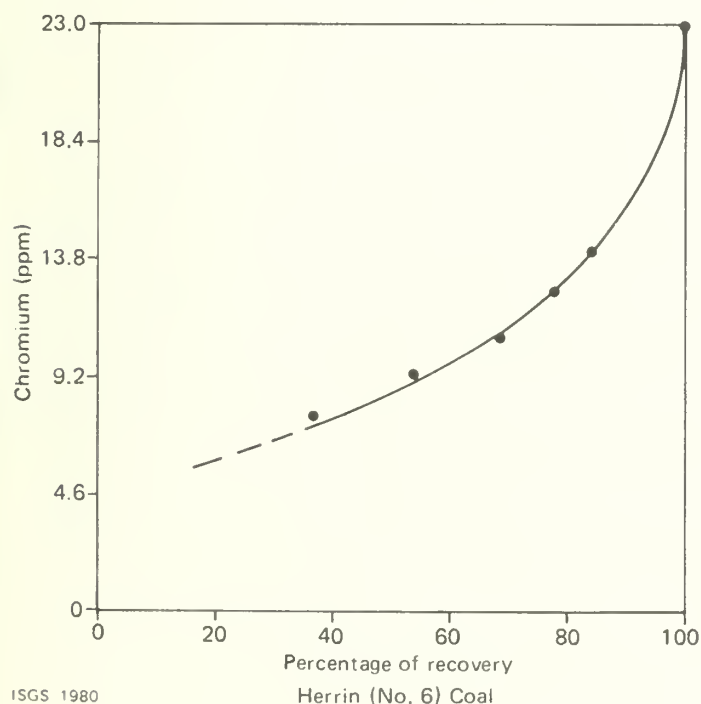
SUMPCT = the cumulative coal recovery percentage,

RECPCT = the coal recovery percentage in the fraction being calculated, and

ANLPPM = the analytical concentration of the element in the fraction being calculated.

This curve (fig. 4) graphs the cumulative concentrations (column 7) versus the cumulative percentage of recovery (column 6) in table 5. For ease of handling the data and for making additional calculations, the washability curve is plotted in a square format in which the lengths of the abscissa and ordinate at 100 percent recovery are equal.

In this case, the washability curve (fig. 4) suggests chromium is principally in the inorganic form; but even the cleanest fraction tested has 8 ppm chromium, and if the curve were extrapolated to the vertical axis, it would intersect well above the origin. The separation of mineral matter from organic matter in specific gravity fractions of coal is not absolute; mineral matter is present in the cleanest (lightest) gravity fraction that could possibly be obtained. Some of the chromium may be present as part of this inseparable mineral matter; therefore, adjustment of the curve for this possible contribution must be made before calculating the area under the curve.



The amount of inseparable mineral matter is assumed to be equal to the percentage of low temperature ash in the lightest gravity fraction. The low temperature ash is determined by radio-frequency ashing at a temperature below 150°C. The other necessary assumption is that the concentration of chromium in the mineral matter (LTA) of the 1.25 float fraction (lightest fraction in this case)

Figure 4. Washability curve for chromium in specific gravity fractions of a sample of the Herrin (No. 6) Coal.

is the same as the concentration of chromium in the mineral matter of the 1.60 sink fraction. This assumption is certainly not as accurate as one would wish because it tends to overestimate the amount of an element contributed by inseparable mineral matter, and therefore, conclusions concerning the amount of organically associated elements (in this case, chromium) are conservative.

An adjusted cumulative curve is constructed after a value (F) for chromium in the inseparable mineral matter is subtracted from each of the concentrations that were determined on the various specific gravity fractions by using the following example of calculations for F:

$$F (\text{inseparable Cr}) = \frac{71 \text{ ppm}}{88.4} \times 3.84 = 3.1 \text{ ppm}$$

3.84 is the percentage of low temperature ash in the lightest (1.25 float) fraction.

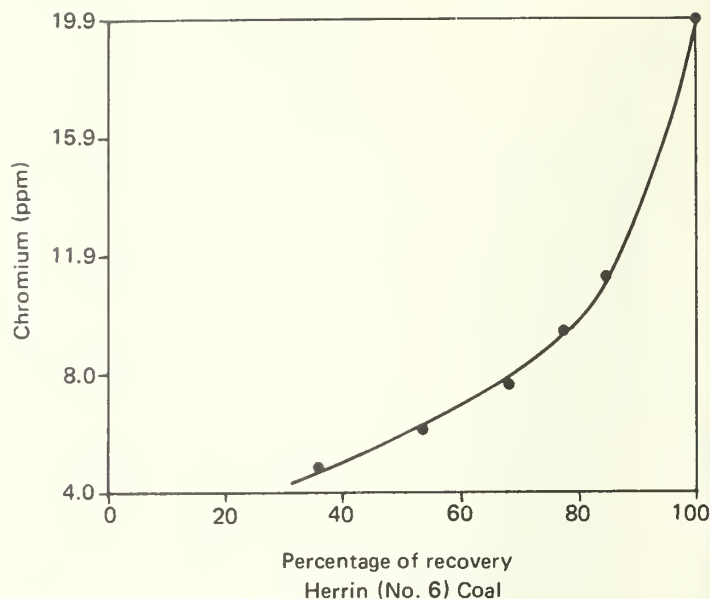
88.4 is the percentage of low temperature ash in the heaviest (1.60 sink) fraction.

71 ppm is the chromium content of the 1.60 sink fraction.

$$\text{CALPPM}(I) = \frac{[(\text{CALPPM}(I-1) \cdot \text{SUMPCT}(I-1))] + [(\text{RECPCT}(I) \cdot (\text{ANLPPM}(I) - F))]}{\text{SUMPCT}(I)}$$

Table 5 lists the normal and adjusted data and the calculated cumulative values from which an adjusted washability curve can be constructed (fig. 5).

The washability curves shown in figures 4 and 5 are very similar. The adjusted curve for Cr (fig. 5) has been "lowered" and the extrapolated intercept of the vertical (zero mineral matter) axis has a lower value. (A constant value for the inseparable mineral matter (3.1 ppm) was subtracted from the concentration in each fraction. However, a more accurate correction may be obtained by subtracting variable amounts based on the percentage of low temperature ash in each gravity fraction.) The total area of the square on which the adjusted washability curve is drawn is defined to have the value of 1.00 at 100 percent recovery. The percentage of that area that lies beneath the curve, expressed as a number with two figures to the right of the decimal is the index of organic affinity. (The significance of a second decimal place has not been determined.) The area under the curve can be determined by constructing a polynomial curve to fit the datum points and



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Figure 5. Adjusted washability curve for chromium in specific gravity fractions of a sample of Herrin (No. 6) Coal.

deriving the value mathematically; or, more simply, a line can be drawn through the points and the area planimeted by hand or by computer methods (digitizer). The digitizer method produced the most reliable results and was used exclusively in this study.

An element that is removed, to any degree, from the clean coal fraction by washing the coal has a value of less than 1.00; for example, see Pb in figure 6. The organic affinity of lead in that sample is 0.08, an extremely low value, indicating that the element is present almost entirely in the mineral-matter fraction.

An element may have an organic affinity greater than 1.00, as in the case for boron in a sample of the Pittsburgh (No. 8) seam from West Virginia (fig. 7). Both standard and adjusted washability curves for B are shown in figure 7. The lighter specific gravity fractions of the coal contain larger amounts of B than the heavier fractions that are rich in mineral matter. Boron is an element that often has a high organic affinity index—in this case, 1.14. Standard and adjusted curves are nearly identical, inasmuch as there is only a minor contribution from the inseparable mineral matter to the total boron content. The organic affinity index is an open-ended scale. The upper limit is dependent only upon the difference between the concentration of the element in the clean coal at the extrapolated Y intercept and the concentration of the element in the coal prior to washing (adjusted end point).

A number of metals have washability curves intermediate between those elements that are generally concentrated in the inorganic fraction (such as zinc) and those that are concentrated in the organic fraction (such as bromine).

Chromium in the Herrin (No. 6) Coal (table 5, figs. 4 and 5) is an example. The adjusted curve intersects the ordinate at a lower value than does the standard curve. But even with the removal of a hypothetical amount of chromium contained in the inseparable mineral matter, there is still an appreciable amount of chromium left in the cleanest, organic-rich coal fractions. The calculated organic affinity of chromium in this sample is 0.37.

Precision and Accuracy of Organic Affinity

There are many potential sources of errors in the analyses and calculations leading to an index of organic affinity. The washability data (percentage of total coal in each specific gravity fraction), the chemical analyses for the element or other constituent, and the amount of low temperature ash in the various fractions are all used in making the calculation; any error in their determinations affects the organic affinity values.

One set of values exists with which the results can be tested. Varieties of sulfur (pyritic sulfur, organic sulfur, and sulfate sulfur) as well as total sulfur had been determined on fractions of washed coal samples. The percentage of sulfate sulfur is very low and generally does not make a significant contribution to the total sulfur content of a fresh coal sample. If analyses for varieties of sulfur were precise and accurate, if measurements of the amount of coal in each washability fraction were accurate, and if measurements of the amount of low-temperature ash were accurate, a perfect correlation should result between organic affinity of total sulfur and percentage of organic sulfur in the total sulfur.

This relationship is shown for the nine coals in figure 8. The agreement is generally good and well within analytical error for determining those

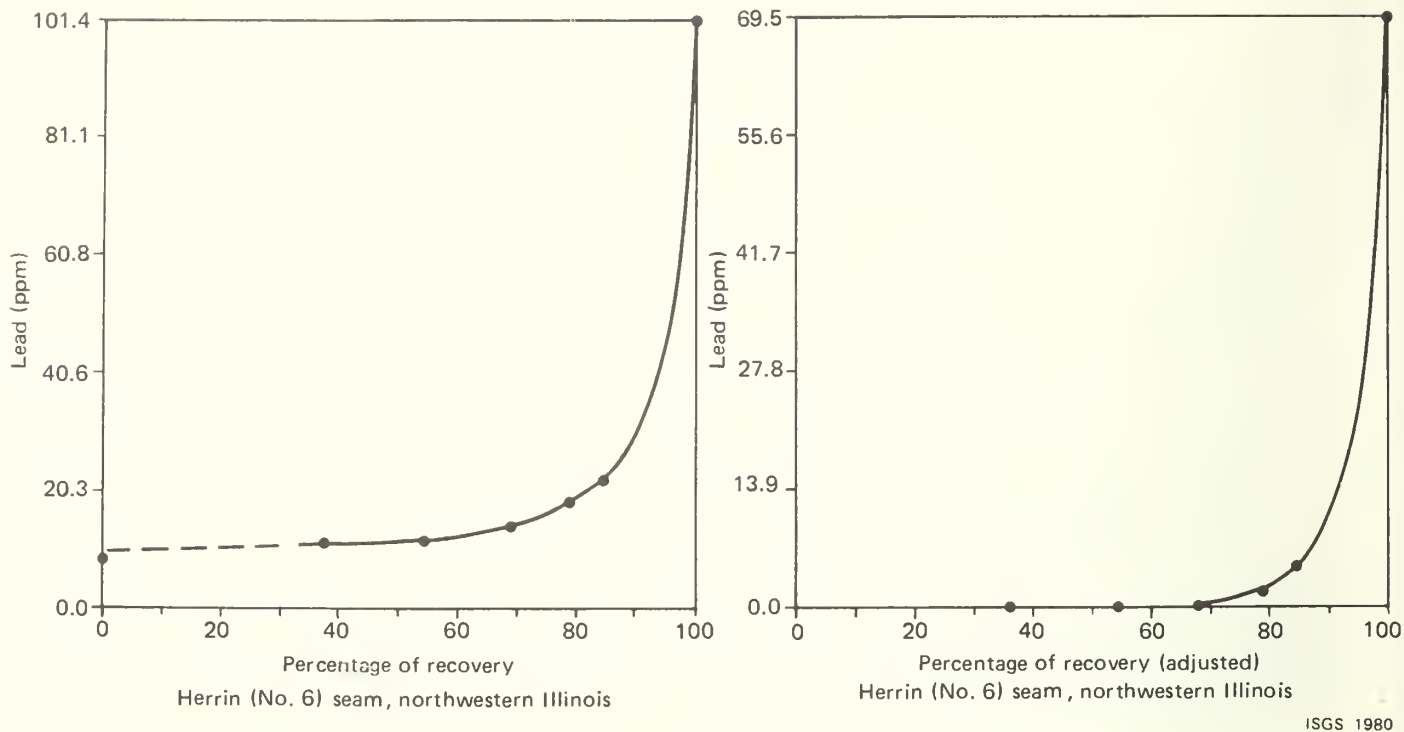


Figure 6. Washability curves for lead in specific gravity fractions of a sample from the Herrin (No. 6) seam. Left: Standard washability curve. Right: Adjusted washability curve.

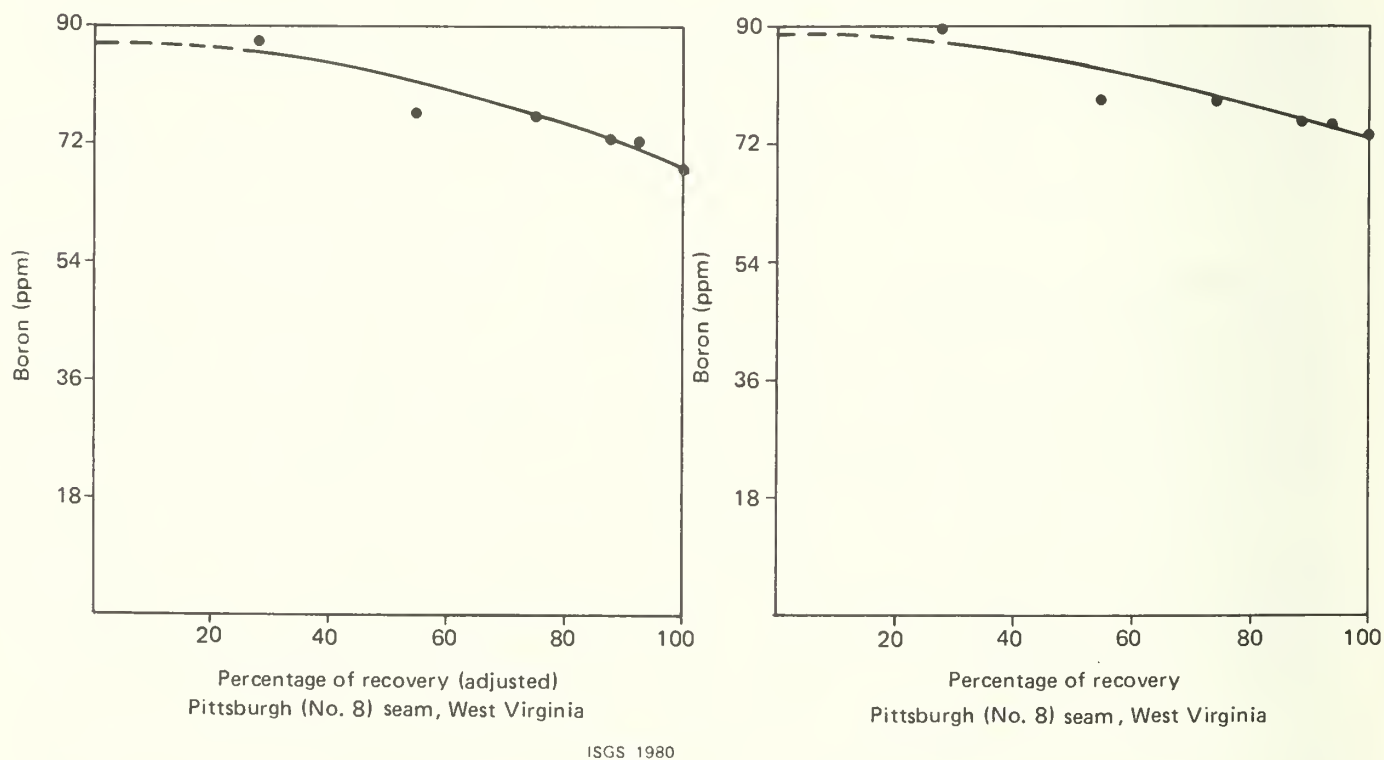


Figure 7. Washability curves for boron in specific gravity fractions of a sample from the Pittsburgh (No. 8) seam from West Virginia. Left: Standard washability curve. Right: Adjusted washability curve.

factors mentioned above for eight of the nine coals analyzed. One point representing a sub-bituminous coal from Montana is anomalous. It arises from the unusual washability characteristics of this coal with regard to total sulfur. Virtually all of the pyritic sulfur in the raw coal sample was removed in the 1.60 sink fraction and there was no detectable pyritic sulfur present in the lighter fractions. Therefore, the assumption, made during the calculation of the organic affinity, that the concentration of sulfur in the inseparable mineral matter of the heaviest and lightest fractions were the same, was invalid. In this case the organic affinity calculated on the unadjusted washability curve is more nearly correct. The knowledge that such anomalies exist contributes to better interpretation of such data and the organic affinity index.

MINERALOGIC METHODS

Qualitative mineralogic analyses of 26 of the 27 raw coals and detailed mineralogic studies of single samples of nine raw coals (see table 1) and their various specific gravity fractions were conducted in conjunction with chemical analyses. The samples were characterized by x-ray diffraction analyses and microscopic examination of low-temperature-ash (LTA) residues prepared from the coal. The original minerals contained in the coal were retained by this radio-frequency plasma ashing technique. Because temperatures are sufficiently low (<150°C), the mineral phases are not significantly altered by oxidation, dehydration, or decomposition (Gluskoter, 1965). Semi-quantitative mineralogic analyses of the major nonclay minerals using an internal standard and prepared calibration curves were carried out by methods adapted from Ward (1977) and Russell and Rimmer (1979). Mineral phases in the LTA in quantities of <1 percent were generally not detectable above background intensities. The total clay percentage was obtained by subtraction. Clay mineral analysis of the <2 μm fraction was conducted using the preparation and analytical methods of Stepusin (1978).

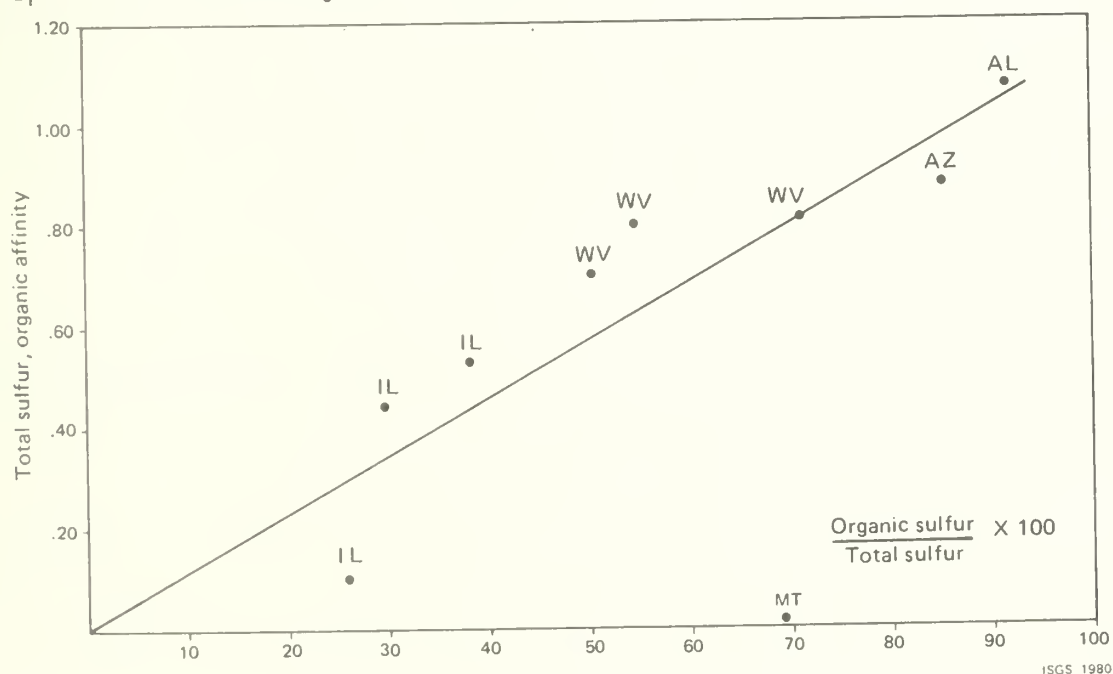


Figure 8. Organic affinity index for total sulfur and the ratio of organic to total sulfur in nine washed coal samples.

SECTION IV

RESULTS

WHOLE COAL AND DEMINERALIZED COAL

Twenty-seven samples of coal, collected from three geographical areas of the United States, were prepared, demineralized, and analyzed as previously described. Of these samples, six were from the eastern region, six from the western region and fifteen from the Illinois Basin. Whole coal, 1.40 float material, nitric acid digested material, and the demineralized product from the 1.40 gravity separation were all analyzed for major and minor ash-forming elements and for trace elements. Of the analytical results, those for whole coal and "mineral-matter-free" coal are most significant to this study. These are presented in table 6. The whole coal values were calculated to the moisture-free basis. The organic portion of the 1.40 gravity separation is assumed to be equivalent to the organic portion of the whole coal, i.e., only the mineral matter content is affected by the separation. Percentage retention of the elements was calculated, and it is also presented in table 6. When the concentration of the element retained was below the detection limit, no percentage was calculated. If the detection limit is approached for both the whole coal and the mineral-matter-free product, the resulting retention percentage may be subject to considerable error, e.g., ± 100 percent.

Table 7 presents the mean elemental concentrations for the whole coals and the demineralized material from the different geographical regions represented. For the purpose of simplicity the coals were divided into three regions; however, an inspection of the standard deviation of the values will indicate that for some elements the variation between samples from the same region is greater than the variation between regions. The implications of this fact will be discussed later.

CONCENTRATIONS OF ORGANICALLY ASSOCIATED ELEMENTS

Table 8 identifies the coals and lists the specific gravity fractions that were obtained from the nine coals used in this portion of the project. Data from these float-sink sets have been used to calculate the relative organic affinities and the elemental concentrations for the whole coals when the adjusted washability curves are extrapolated to 0 percent recovery (tables 9-17). The analytical data for the individual gravity fractions in table 8 are not given because data are so extensive and have been reported in Gluskoter et al. (1977), p. 90-104, except for set 4 from sample 18841 and set 8 from sample C19854. The results for these two sets are given in Kuhn et al. (1978), p. 5-8.

(text continues on page 43)

TABLE 6. Comparison of concentrations of trace and minor elements in raw and demineralized (MMF) coal

Sample no.	Si			Al			Fe			Ca		
	Raw coal (%)	MMF* (ppm)	Retention † (%)	Raw coal (%)	MMF* (ppm)	Retention † (%)	Raw Coal (%)	MMF* (ppm)	Retention † (%)	Raw coal (%)	MMF* (ppm)	Retention † (%)
C-18126	2.48	36	0.1	1.12	60	0.5	1.83	55	0.3	.73	13	.2
C-16543	2.06	39	.2	1.51	65	0.4	1.59	93	0.6	2.67	28	.1
C-16993	3.47	69	0.2	1.05	73	0.7	2.96	58	0.2	0.63	51	.8
C-17001	2.08	197	1.0	0.86	125	1.4	2.76	64	0.2	0.82	67	.8
C-18304	3.31	53	.2	1.72	199	1.2	2.79	100	0.4	0.17	200	12
C-18560	3.20	41	0.1	1.40	41	.3	2.60	66	0.3	0.51	25	.5
C-18704	2.50	57	0.2	1.70	41	0.2	0.63	143	2.3	1.00	14	.1
C-18816	1.92	51	.3	1.54	41	.3	0.60	60	1.0	0.83	44	.5
C-18820	2.51	56	0.2	1.41	169	1.2	0.56	72	1.3	0.56	74	1.3
C-18841	2.34	64	.3	1.23	282	2	1.73	242	1.4	0.53	213	4
C-18848	2.80	64	0.2	1.90	236	1.2	0.70	54	0.9	0.35	48	1.4
C-18857	2.80	48	.2	1.10	67	0.6	2.20	67	0.3	0.48	27	.6
C-19000	0.71	53	0.7	1.40	187	1.3	0.40	225	5.6	0.46	199	4.3
C-18571	1.50	44	.3	0.85	65	0.8	3.80	113	0.3	2.70	85	.3
C-18844	1.90	76	0.4	1.20	82	0.7	1.30	146	1.1	0.55	38	.7
C-19824	1.95	40	0.2	1.02	41	0.4	1.12	80	0.7	1.61	30	.2
C-19854	2.41	30	0.1	1.15	20	0.2	.47	35	0.8	0.97	20	.2
C-18824	3.00	63	.2	2.00	57	.3	.61	46	.8	.15	21	1.4
C-18440	1.30	88	.7	.89	71	.8	.33	22	.7	1.70	31	.2
C-18748	1.00	60	.6	.43	65	.02	.57	12	.2	.22	31	1.4
C-18320	3.20	60	.2	1.60	48	1.5	1.81	55	.3	.88	46	.5
C-18368	2.90	44	.1	1.40	44	.3	2.10	50	.2	.62	41	.7
C-18445	1.33	45	.3	.99	58	.6	.38	30	.8	2.10	58	.3
C-18457	.71	69	1.0	.36	78	2.2	.21	56	2.7	3.89	16	<.1
C-14684	2.12	98	.5	1.18	82	.7	.69	120	1.7	.54	19	.3
C-15999	3.01	81	.3	1.57	77	.5	1.78	75	.4	.21	41	.8
C-16173	1.92	52	.3	.92	65	.7	1.60	67	.4	.56	64	1.1

*Concentration in the demineralized residue of the 1.40 float fraction of the coal.

†Concentration in the mineral-matter-free (MMF) coal divided by the concentration in the raw coal.

TABLE 6. *Continued*

Sample no.	Na			Mg			K			Ti		
	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (%)	MMF* (ppm)	Retention† (%)	Raw coal (%)	MMF* (ppm)	Retention† (%)	Raw coal (%)	MMF* (ppm)	Retention† (%)
C-18126	200	6.6	3.3	0.05	43	8.6	0.17	1.3	0.1	0.07	20	2.9
C-16543	405	6.6	1.6	0.04	33	8.2	0.14	1.3	0.1	0.08	22	2.7
C-16993	280	8	2.9	0.07	40	5.7	0.20	40	2.0	0.12	20	1.7
C-17001	700	25	3.6	0.02	95	47.5	0.14	31	2.2	0.06	19	3.2
C-18304	200	20	10.0	0.04	29	7.2	0.13	<2		0.10	60	6.0
C-18560	400	6	1.5	0.06	21	3.5	0.13	<1		0.06	20	3.3
C-18704	1820	15	0.8	0.16	37	2.3	0.21	14	0.6	0.12	40	3.3
C-18816	170	<3		0.10	14	1.4	0.02	<10		0.07	27	3.9
C-18820	700	0.5	.1	0.06	18	3.0	0.23	<10		0.12	199	16.6
C-18841	730	6	0.8	0.04	7	1.7	0.25	0.7	0.03	0.06	94	15.7
C-18848	338	<3		0.05	<20		0.29	2.3	0.1	0.15	28	1.9
C-18857	950	4	0.4	0.05	<20		0.17	<1		0.06	16	2.7
C-19000	1650	1.4	.1	0.07	<20		0.02	<10		0.06	54	9.0
C-18571	125	<3		0.05	20		0.07	<5		0.03	21	7.0
C-18844	260	6	2.3	0.04	<20		0.14	<10		0.08	81	10.1
C-19824	676	8.8	1.3	0.16	<20		0.09	2.5	0.2	.06	11	1.9
C-19854	191	15	7.8	0.44	<20		0.09	<5	0.6	.06	4	0.7
C-18824	180	30	16.7	.03	49	16	0.12	<1		.12	45	3.7
C-18440	3550	4	.1	.28	<20		0.03	<1		.02	39	19.5
C-18748	230	3.5	1.5	.04	<20		0.37	4.6	.1	.07	27	3.8
C-18320	700	.8	.1	.07	<20		0.19	7	.3	.07	29	4.1
C-18368	244	4	1.6	.05	17	3.4	0.20	1	.05	.07	29	4.1
C-18445	110	<2		.19	23	1.2	0.01	<1		.05	33	6.6
C-18457	90	11	1.2	.12	15	1.3	0.02	<1		.02	30	15.0
C-14684	640	1.0	.2	.04	21	5.2	0.13	<1		.08	58	7.2
C-15999	236	6.0	2.5	.05	18	3.6	0.23	1	.04	.08	56	7.0
C-16173	351	<2		.05	15	3.0	0.11	<1		.05	28	5.6

*Concentration in the demineralized residue of the 1.40 float fraction of the coal.

†Concentration in the mineral-matter-free (MMF) coal divided by the concentration in the raw coal.

TABLE 6. Continued

Sample no.	P			Mn			S			Organic S		
	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (%)	MMF* (%)	Retention† (%)	Raw coal (%)	MMF* (%)	Retention† (%)
C-18126	21	1.4	6.7	76	0.3	.4	3.25	1.12	34.5	1.15	1.12	97
C-16543	24	0.1	0.4	93	0.8	.9	3.15	1.93	61.3	1.91	1.93	101
C-16993	84	2.5	3.0	75	0.5	.7	4.15	1.76	42.4	1.65	1.76	107
C-17001	48	2.8	5.8	18	0.7	3.9	4.14	1.57	37.9	1.51	1.57	104
C-18304	192	2	1.0	20	0.8	4	3.59	1.07	29.8	.99	1.07	108
C-18560	50	<1		62	0.3	.5	6.45	1.81	28.1	1.87	1.81	97
C-18704	76	11	14.4	146	0.4	.3	2.63	2.00	76.0	2.08	2.00	96
C-18816	76	3	4.0	32	2.1	6.5	1.00	0.45	45.0	.45	.45	100
C-18820	26	0.1	.4	14	0.5	3.6	0.79	0.47	59.5	.50	.47	94
C-18841	59	2	3.4	20	3.7	18	5.01	2.28	45.5	2.35	2.28	97
C-18848	190	<4		13	<1		0.55	0.33	60.0	.36	.33	92
C-18857	31	7	22.6	54	0.4	0.7	5.02	2.30	45.8	2.25	2.30	102
C-19000	120	<4		8	0.4	4.8	0.61	0.32	52.5	.38	.32	84
C-18571	62	4	6.4	260	0.3	0.1	6.10	1.71	28.0	1.80	1.71	95
C-18844	68	5	7.3	10	0.3	3.0	2.30	1.15	50.0	1.20	1.15	96
C-19824	103	<5		35	0.68	1.9	2.23	1.18	52.9	1.15	1.18	103
C-19854	121	<5		85	1.5	1.7	0.90	0.46	51.1	.58	.45	97
C-18824	62	4	6.4	29	6.7	23.1	.98	.56	57.1	.54	.56	83
C-18440	150	<2		52	6.1	11.7	.51	.43	84.3	.47	.43	91
C-18748	158	11	7.0	120	5.1	4.2	.92	.36	39.1	.38	.36	95
C-18320	52	8	15.4	37	4	10.8	3.56	1.98	55.6	1.87	1.98	106
C-18368	25	1	4.0	13	.3	2.3	3.93	1.93	49.1	2.07	1.93	93
C-18445	90	2	2.2	112	.5	.4	.83	.61	73.5	.59	.61	103
C-18457	16	<1		42	.2	.5	.54	.27	50.0	.25	.27	108
C-14684	75	5	6.7	34	.3	.9	1.40	.65	46.4	.72	.65	90
C-15999	10	3	30.0	15	.32	2.1	3.31	1.36	41.1	1.38	1.36	99
C-16173	110	2	1.8	191	.74	.4	3.52	2.03	57.7	2.14	2.03	95

*Concentration in the demineralized residue of the 1.40 float fraction of the coal.

†Concentration in the mineral-matter-free (MMF) coal divided by the concentration in the raw coal.

TABLE 6. Continued

Sample no.	Be			B			Sc			V		
	Raw coal (ppm)	MMF* (ppm)	Retention † (%)	Raw coal (ppm)	MMF* (ppm)	Retention † (%)	Raw coal (ppm)	MMF* (ppm)	Retention † (%)	Raw coal (ppm)	MMF* (ppm)	Retention** (%)
C-18126	2.8	0.03	1	100	6.6	6.6	3.5	.13	4	32	8.5	26
C-16543	2.4	0.04	2	81	7.7	9.5	3.1	.11	3	32	9.2	28
C-16993	1.3	0.02	1	81	6.6	8.1	2.6	.2	8	54	2	4
C-17001	1.6	0.06	4	37	6.1	1.6	2.9	.9	31	62	1.6	2
C-18304	2.2	0.11	5	68	11	16.2	3.0	.04	1	34	3	9
C-18560	1.4	0.03	2	200	6.6	3.3	4.1	.65	16	34	3.5	10
C-18704	0.7	0.03	4	264	10	3.8	2.7	.5	18	83	17	20
C-18816	0.49			66	5.5	8.3	1.8	.2	11	31	1	3
C-18820	0.88	0.11	12	12	9.7	80.8	5.5	2.0	36	62	1.5	2
C-18841	0.66	0.01	1	120	24	20.0	4.8	1.3	27	32	4	12
C-18848	0.68	0.05	8	15	5.1	34.0	8.0	2.5	31	77	<5	
C-18857	1	0.05	5		8.8		3.2	.5	16	32	<5	
C-19000	0.39	0.03	8	37	5.3	14.3	1.6	.42	26	8	<5	
C-18571	2.9	0.13	4	110	8.5	7.7	1.5	.25	17	18	<5	15
C-18844	0.58	0.05	9	48	16	33.3	1.8	.62	34	42	6.5	
C-19824	0.45	0.07	2	82			2.3	.08	3	17	2.7	16
C-19854	0.47	0.03	6	100			1.6	.6	37	11	1.2	11
C-18824	1.0	.08	8	40	13	32.5	7	1.2	17	60	32	53
C-18440	.55	.01	2	44	18	40.9	1.2	.09	7	31	5.2	17
C-18748	2.6	.14	5	18	12	66.7	4.7	1.6	34	173	1.5	1
C-18320	1.1	.02	2	230	8.3	36.1	3.5	.7	20	34	1.1	3
C-18368	1.0	.03	3	210	8.3	39.5	3.7	.5	13	32	4	12
C-18445	.20	.08	40	91	5.7	6.2	1.4	.1	7	20	2.1	10
C-18457	.31	.009	3	16	2.2	13.8	.8	.36	45	2.6	2.1	80
C-14684	.80	.02	2	33	4.9	14.8	1.9	.55	29	33	6	18
C-15999	1.5	.03	2	82	7.7	9.4	3.0	1.0	33	36	7	19
C-16173	.96	.05	5	241	13	5.4	1.7	.37	22	23	7	30

*Concentration in the demineralized residue of the 1.40 float fraction of the coal.

†Concentration in the mineral-matter-free (MMF) coal divided by the concentration in the raw coal.

TABLE 6. Continued

Sample no.	Cr			Co			Ni			Cu		
	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)
C-18126	32	5.2	16	7.7	0.2	3	32	<3		20	4.1	20
C-16543	14	5.4	38	13	0.4	3	23	5	23	16	4.1	25
C-16993	17	.5	3	3.9	0.2	5	12	<5		12	6.5	54
C-17001	15	<5		2.0	<1		17	<4		8	1.8	22
C-18304	19	5.0	26	4.0	0.6	15	14	1	8	18	<0.3	
C-18560	20	7	34	7.2	0.4	6	24	<1		17	2.1	12
C-18704	42	7	17	3.5	0.3	9	37	<3		31	4.3	14
C-18816	13	1.2	9	2.5	0.6	24	8.5	<2		27	7.7	28
C-18820	20	6.3	31	7.5	5.4	72	12	<5		29	6.5	22
C-18841	17	8.6	50	2.9	0.8	28	14	3	22	16	<0.3	
C-18848	26	14	54	18	10	55	15	1	7	24	4.1	17
C-18857	33	7	21	4	0.3	7	14	<1.5		16	<3.0	
C-19000	3.4	1.4	41	1.1	0.5	45	2.6	<1.5		2	<3.0	
C-18571	36	3.7	10	6.5	0.6	9	18	<2	46	17	<0.3	
C-18344	15	6.1	41	1.7	0.8	47	6.4	3		24		
C-19824	14	2.0	14	2.2	0.2	10	13	2		9	1.5	17
C-19854	6.2	0.6	10	2.0	1.5	75	3	<2		9	1.8	20
C-18824	31	6.7	22	8.6	3.7	43	13	5	38	32	3.0	9
C-18440	8.4	.8	9	1.0	.1	12	4	<2		14	2.3	16
C-18748	22	8	36	5.9	.9	15	20	5	25	26	.3	1
C-18320	50	12	24	3.7	.4	11	20	14	70	34	3.6	10
C-18368	47	6	13	4.0	.5	12	19	2	10	16	<.3	
C-18445	9.2	1.8	20	.8	.2	25	2.6	<2		16	<.3	
C-18457	6	1.2	20	.6	.15	25	4.4	<1		14	2.4	17
C-14684	14	4.6	33	3.0	.9	30	12	4	33	8	2.2	27
C-15999	23	7.4	32	5.2	.35	7	15	5	33	36	7	19
C-16173	14	6	43	1.9	.3	17	22	<3		22	12	54

*Concentration in the residue demineralized of the 1.40 float fraction of the coal.

†Concentration in the mineral-matter-free (MMF) coal divided by the concentration in the raw coal.

TABLE 6. *Continued*

Sample no.	Zn			Ga			As			Se		
	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)
C-18126	2668	3	<1	4.5	.7	15	31	<.5		2.4	.37	15
C-16543	5700	<1		4.8	.7	14	8.1	.14	2	2.9	.31	11
C-16993	41	4	10	3.6	.4	11	7.1	<.1		1.7	.72	42
C-17001	27	<1		2.8	.9	32	3.3	<.5		2.4	<.5	
C-18304	27	<1		2.6	<.2		5.4	<.1		3.3	.7	21
C-18560	57	1		2.4	.7	29	3.4	<.07		4.3	.3	7
C-18704	31	<1	2	3.5	.6	17	8.1	<1.0		2.4	.2	8
C-18816	13	<1		4.3	.1	2	5.3	<.3		2.1	.2	9
C-18820	12	<1		4.2	.7	17	15.0	<.5		5.8	1.0	17
C-18841	14	<1		4.3	1.7	39	3.2	<.5		1.1	.4	36
C-18848	2	<1.0		6.3	.1	1	1.8	<.1		3.0	.5	17
C-18857	50	<1		2.7	.6	22	2.3	<.1		3.6	.2	5
C-19000	3	<0.5		2.3	.1	4	1.1	.2	18	1.6	.6	37
C-18571	17	<5		3.6	.6	17	4.6	<.1		2.5	.29	12
C-18844	16	<5		3.2	1.6	50	15	<1.0		2.1	.6	28
C-19824	10	<1		2.6	1.4	54	3.9	.3	7	1.6	.5	31
C-19854	4	<0.3		3.3	2.2	67	.7	<.3		.9	.34	37
C-18824	120	<4		7.4	1.4	19	22	<.1		5.0	.5	10
C-18440	<4	<2		4.2	.4	9	1.8	.9	50	1.4	.7	50
C-18748	26	<5		5.8	.2	3	230	<.7		2.4	.26	11
C-18320	60	<5		2.5	.7	28	2.1	<.5		4.0	.6	15
C-18368	75	<2		2.8	.6	21	2.7	<.5		2.7	.3	11
C-18445	6	<2		1.5	1.2	80	.8	.4	50	1.3	.2	15
C-18457	24	<5		.76	.4	50	1.2	.5	42	1.0	.3	32
C-14684	13	<1		2.2	.5	23	4.6	.2	4	1.3	.3	22
C-15999	75	<5		4.0	.8	21	3.1	<.1		1.6	.28	17
C-16173	1200	<5		1.6	.3	22	4.5	<.5		2.0	.27	13

*Concentration in the demineralized residue of the 1.40 float fraction of the coal.

†Concentration in the mineral-matter-free coal divided by the concentration in the raw coal.

TABLE 6. Continued

Sample no.	Br			Rb			Sr			Mo		
	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)
C-18126	16	6.3	39	14	<1		19	<1.0		9.1	<1	
C-16543	8	3.6	45	8.7	<1		23	2	9	5.8	<1	
C-16993	17.5	16	91	14.5			27	10	37	<1.0	<1	
C-17001	23	24	100	25	<1		17	8	47			
C-18304	16	7.4	46	20	<1		95	15	10	2.4		
C-18560	3.4	3.3	97	23	<1		33	1.5	4	11	0.5	5
C-18704	6.6	4.2	64	32	<1		37	3.0	8	1.5	<1	
C-18816	0.5	0.6	100	1.5	<1		244			<1		
C-18820	24	16	67	16	<1		126	50	40	4.6	<1.0	
C-18841	10	3.8	38	13	<1		105			1.1		
C-18848	2.5	1.7	68	18	<1		122	13	11	6.2		
C-18857	5	4	80	22	<1		30	3	10	6.1	<1.0	
C-19000	0.9	1		1.2	<1		204			<1.0		
C-18571	2.6	1.7	65	8.3	<1		55			16	1.8	11
C-18844	18	20		10	<1		140			<1.0		
C-19824	12	12	100	9.5	<1		200	24	12	<2	<0.2	
C-19854	1.6	4.5		3.3	<1		95	4.4	5	7.1	1.4	20
C-18824	1.7	4.8		17			35	<5		12	<5	
C-18440	1.0	3.5		1.32	<1	6	240	<5		<1		
C-18748	39	24	61	47	3		80	<3				
C-18320	13	3.0	23	14	<1		40			6.3	<.5	9
C-18368	1.8	1.1	60	23	<1		33			6.8	.6	
C-18445	1.5	.82	55	<1			108			3.3		
C-18457	1.2	.1	8	1.9	<1		218	3.7	2	.8	<.5	
C-14684	23	9.2	40	15	<1		40	3.5	9	1.4	<.5	8
C-15999	8.5	6.0	71	17	<1		23	5.5	24	7.8	.6	
C-16173	1.8	1.2	67	10	<1		16	<1		2.6		

*Concentration in the demineralized residue of the 1.40 float fraction of the coal.

†Concentration in the mineral-matter-free (MMF) coal divided by the concentration in the raw coal.

TABLE 6. Continued

Sample no.	Cd			Sb			Cs			Ba		
	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)
C-18126	28	.1	.4	4.2	.6	15	1.0	<.01		80	2.2	3
C-16543	65	1.1	2	2.2	1.2	54	1.0	.03	3	750	<2	
C-16993	<.4	<.4		.36	<.03		.9	<.04		48	2.6	6
C-17001	2.5	1.2	48	4.7	.6	13	1.6	<.1		86	3.0	3
C-18304	<.4	<.4		.35	<.03		1.0	.1	10	41	3.3	8
C-18560	<.1	<.1		.5	.1	18	2.0	.1	5	54	<2	
C-18704	<.3	<.3		.65	.2	29	2.3	<.1		1500	1.5	.1
C-18816	.2	<.1		3.5	.4	11	.3	<.02		460	6	
C-18820	<.1	<.1		4.6	.6	13	2.0	.2	10	180	33	18
C-18841	<.1	<.1		.25	.1		1.0	.03	3	72	10	14
C-18848	<.1	<.1		1.5	.7	48	2.3	.05	2	230	20	9
C-18857	.2	<.1		.42	.1		1.6	<.1		60	<5	
C-19000	<.1	<.1		.4	.2	50	.11	<.05		265	15	6
C-18571	<.1	<.1		.20	<.08		.77	<.01		90	4	4
C-18844	<.1	<.1		.51	.1	29	.9	<.01		87	13	15
C-19824	.24	<.1		6	.8	14	.76	.03	4	130	27	21
C-19854	.22	<.07		1.0	.7	73	.43	<.04		808	40	5
C-18824	<.2	<.2		2.6	.1	38	1.2	<.02		180	16	9
C-18440	<.1	<.1		.9	.6	66	.06	.01	17	500	8.1	2
C-18748	<.2	<.2		1.2	.2	17	2.6	.2	8	96	<2	
C-18320	.3	<.1		.54	.3	56	.93	.01	1	46	2.8	6
C-18368	.3	<.1		.5	.1	24	2.6	.05	2	92	5.9	6
C-18445	<.1	<.1		.61	.3	56	.06	<.01		495	5	1
C-18457	<.1	<.1		.4	.1	35	.16	<.05		460	2.6	.6
C-14684	<.2	<.2		1.2	.3	62	.96	.01	1	40	4.2	10
C-15999	1.8	.3	16	1.1	.4	35	1.2	<.1		23	4.6	20
C-16173	.4	<.2		1.0	.5	47	.4	.02	5	63	1.8	3

*Concentration in the demineralized residue of the 1.40 float fraction of the coal.

†Concentration in the mineral-matter-free (MMF) coal divided by the concentration in the raw coal.

TABLE 6. Continued

Sample no.	La			Ce			Sm			Eu		
	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)
C-18126	5	.5	10	5.0	.7	15	.86	.17	20	.2	.03	15
C-16543	6.1	.5	8	8.6	.7	8	.73	.16	22	.2	.03	15
C-16993	9.3	.4	5	11.4	1.1	10	.93	.23	25	.31	.04	13
C-17001	6.5	.9	14	16	1.9	12	1.3	.3	23	.21	.06	28
C-18304	5.6	2.0	36	14	4	29	1.4	.5	36	.35	.05	14
C-18560	6.1	.7	12	25	1.7	7	.86	.41	48	.3	.1	28
C-18704	9.4	.5	5	20	.9	4	1.7	.2	12	.3	.05	17
C-18816	8.5	2.5	29	13	2.7	21	.9	.4	44	.21	.05	23
C-18820	20	5.0	25	31	4.5	14	2.6	.9	35	.5	.2	40
C-18841	8.7	2.4	28	15	3.3	22	1.5	.6	40	.26	.12	54
C-18848	18	2.8	16	30	3.5	12	2.8	.06	2	.53	.1	21
C-18857	5.7	.5	9	8	1	12	.9	.22	24	.20	.05	25
C-19000	6.0	1.3	22	6	1.2	20	.8	.3	37	.15	.05	33
C-18571	5.0	.8	16	12	1.1	9	1.4	.45	32	.38	.08	21
C-18844	7.2	1.7	24	11	3.1	28	2.8	.40	14	.26	.15	58
C-19824	5.7	2.6	46	16	2.5	16	.9	.47	50	.22	.06	27
C-19854	5.2	1.3	25	10	3.3	32	.9	.25	29	.15	.04	27
C-18824	18	2.0	11	25	2.5	10	2.7	.8	30	.6	.09	15
C-18440	5.7	.4	7	8.5	.6	7	.5	.09	18	.30	.08	27
C-18748	26	2.0	8	42	3	7	3.3	.4	12	.0	.09	10
C-18320	5.8	1.0	17	25	1.7	7	1.4	.35	25	.30	.08	27
C-18368	7.1	1.1	15	27	1.7	6	1.5	.5	33	.34	.10	29
C-18445	4.2	1.3	31	12	1.3	11	.6	.1	17	.11	.02	18
C-18457	4.3	1.0	23	8.6	1.2	14	.45	.12	27	.1	.04	40
C-14684	7.5	.8	11	11	.4	4	.84	.19	23	.17	.04	23
C-15999	12	.6	5	18	1.1	6	1.6	.22	14	.38	.06	16
C-16173	2.9	.7	25	5.6	1.2	21	.38	.19	50	.07	.02	29

*Concentration in the demineralized residue of the 1.40 float fraction of the coal.

†Concentration in the mineral-matter-free (MMF) coal divided by the concentration in the raw coal.

TABLE 6. *Continued*

Sample no.	Tb			Dy			Yb			Lu		
	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)
C-18126	.21	.07	33	1.1			.7	.07	10	.1	.02	20
C-16543	.18	.07	39				.59	.08	13	.08	.02	25
C-16993	.2			1.3	.2	15	.53	.07	13	.07	.01	14
C-17001				.8	.4	50	.5	.2	40	.09	<.01	
C-18304				1.3	.4	31	.9	.2	22	.19	.03	16
C-18560	.45	.1		1.4	.4	28	.84	.23	27	<.02	<.01	
C-18704	.2	<.08		.8	.2		.45	.10	22	.08	.02	25
C-18816	.17	.05		.93			.61	.13	21	.09	.03	33
C-18820	.26	<.1		2	.9	45	.75	.20	26	.18	.05	27
C-18841	.14	<.1		1.6			.5	.20	40	<.1	.05	
C-18848	.22	<.1		2.4	.7	29	.80	.25	31	.10	.07	70
C-18857	.22	.08	36	.6	.2	33	.27	.10	37	.10	.02	20
C-19000	.08	<.05		.65			.24	.11	46	.08	.03	37
C-18571	.45	.08	17	1.3			.67	.13	19	.07	.03	43
C-18844	.10	<.10		.8			.29	.2	68	.04		
C-19824	.13	.04	31	.8	.4	48	.30	.13	43	.08	.02	25
C-19854	.13	.05	38	.6	.2	38	.32	.19	59	.06	.03	50
C-18824	.35	<.2		2.4			.83	.4	48	.25	.10	40
C-18440	.18	<.1		.5			.55	.09	16	<.3		
C-18748	.62	.12	19				.87	.20	23	.34	.05	15
C-18320	.41			.95	.33	35	.84	.22	26	.12	.04	33
C-18368				.72			.77	.18	23	.15	.03	20
C-18445	.18	<.1		.38			.37	.06	16	<.02	.01	
C-18457				.51	.18	35	.26	.06	23	.06	.01	17
C-14684	.18	<.05		.82	.25	30	.39	.15	38	.05	<.02	
C-15999	.21	<.1		1.9	.4	21	.72	.21	29	.11	.04	36
C-16173	.2	<.06		.27	.10	37	.26	.07	27	.08	.03	12

*Concentration in the demineralized residue of the 1.40 float fraction of the coal.

†Concentration in the mineral-matter-free (MMF) coal divided by the concentration in the raw coal.

TABLE 6. Continued

Sample no.	Hf			Ta			W			Pb		
	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)
C-18126	.62	.02	3	.11	.04	36	.5	.06	12	72	<1	
C-16543	.5	.03	6	.17	<.02		.41	<.05		37		
C-16993	.43			.2	<.04		1.6	.6	37			
C-17001	1.0			.06	<.01		.9	.5	55			
C-18304	1.3	.2	15	.20	.03	15	.8	.08	10	22		
C-18560	1.1	.11	10	.25			.6	.06	10	<1	<1	
C-18704	.64	.09	14	.15	.03	20	.6	<.2		11		
C-18816	.9	.16	18	.16			.7	.04	6	4.0		
C-18820	1.5	.2	13	.70	.09	13	.5	.12	24	1.6		
C-18841	1.0	.12	12	.77			.4	.06	15	3		
C-18848	1.8	.33	18	.12			.3	<.1		12		
C-18857	.70	.10	14	.14	.05	35	.4	<.1		<1	<1	
C-19000	.64	.20	31	.10			1.2	<.3		<0.7	<0.7	
C-18571	.35	.06	17	.10			1.4	<.05		68		
C-18844	1.0	.33	33	.15			.6	.15	25	3.9		
C-19824	1.0	.6	60	.17	.08	47	.3	<.09		25	<1	
C-19854	1.2	.2	17	.13	.07	54	.7	<.06		4.6	<1	
C-18824	1.7	.16	9	.3	.09	30	1.3	.7	53	7.6	<1	
C-18440	.9	.40	44	.20	.11	55	1.1	.4	36	5.5	<1	
C-18748	1.4	.32	23	.28	.12	43	3.0	1.3	43	20	<1	
C-18320	1.0	.12	12	.26	<.05		.5	<.1		4.0	<1	
C-18368	.8	.08	10	.25			.5			5.4		
C-18445	1.1	.30	27	.16			.8	<.1		2.4		
C-18457	1.2	.33	27	.05			.3	<.07		<1		
C-14684	.5	.15	30	.14			.3	.06	20	11		
C-15999	.5	.14	26	.2			.4	<.1		24		
C-16173	1.2	.11	9	.03	<.05		.9	<.1				

*Concentration in the demineralized residue of the 1.40 float fraction of the coal.

†Concentration in the mineral-matter-free (MMF) coal divided by the concentration in the raw coal.

TABLE 6. *Continued*

Sample no.	Th			U			1.40 float (% recovery)
	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	Raw coal (ppm)	MMF* (ppm)	Retention† (%)	
C-18126	2.4	.5	20	3.9	.12	3	78
C-16543	2.2	.5	25	1.7	<.1		79
C-16993	2.0	.4	20	.8	<.1		70
C-17001	2.8	.8	29	2.1	1.6	76	83
C-18304	1.8	.2	11	1.3	.2	15	85
C-18560	3.6	1.0	28	1.9	.09	5	79
C-18704	2	.4	20	7.5	.5	7	74
C-18816	3	1.0	33	1.0	.02	2	
C-18820	6.2	1.1	18	1.0	.2	20	75
C-18841	2.9	.6	21	.73	.07	9	80
C-18848	5.4	.5		.9	.3	33	82
C-18857	1.4	.4	29	.84	<.5		83
C-19000	1.4	.6	43	<.70	.05		92
C-18571	1.37	.2	18	4.9	.3	7	85
C-18844	2.40	.9	37	.4	<.1		89
C-19824	2.1	1.1	52	<.6	<.1		
C-19854	2.5	.7	31	1.5	.2	13	87
C-18824	5.4	1.5	28	2.9	.5	17	79
C-18440	2.7	.6	22	1.0	.3	30	51
C-18748	3.9	1.1	28	1.2			57
C-18320	1.4	.5	36	1.4	.2	14	79
C-18368	3.1	.8	26	1.5	.2	13	80
C-18445	2.9	1.1	38	1.1	<.5		
C-18457	.67			.6	.1	23	
C-14684	1.8	.6	32	.4	.1	29	78
C-15999	2.8	.6	20	1.0	.26	26	76
C-16173	1.0	.3	35	2.0	.25	12	87

*Concentration in the demineralized residue of the 1.40 float fraction of the coal.

†Concentration in the mineral-matter-free (MMF) coal divided by the concentration in the raw coal.

TABLE 7. Mean concentrations and mean retention percentages in mineral-matter-free coals*

Element	IL Herrin (No. 6)			Eastern			Western		
	Raw Coal	MMF	Retention Percentage	Raw Coal	MMF	Retention Percentage	Raw Coal	MMF	Retention Percentage
Si	2.60±.6%	56±19	0.2	2.41±.4%	60±12	0.2	1.39±.7%	56±20	0.4
Al	1.28±.3%	61±14	0.5	1.94±.6%	144±100	0.7	1.06±.4%	76±58	0.7
Fe	1.96±.9%	96±53	0.5	1.0±.5%	107±75	1	0.4±0.1%	71±77	2
Ca	0.96±.8%	38±22	0.4	0.62±.5%	71±72	1	1.66±1.2%	61±69	0.4
Na	592±472	5.8±4	1	481±248	10±11	2	960±1410	7.8±6	0.8
Mg	0.06±.03%	26±10	4	0.06±.05%	25±22	4	0.20±0.1%	17±5	0.9
K	0.16±.05%	9.3±14	0.6	0.19±.09%	1.8±1	0.1	0.03±.03%	—	—
Ti	0.07±0.02%	30±14	4	0.10±.04%	76±68	8	0.05±.02%	31±16	6
P	52±30	4.1±3	8	85±57	2.3±2	3	96±47	—	—
Mn	88±75	0.72±1	0.8	20±10	2.4±3	12	55±38	1.8±2	3
S	3.9±1.4%	1.7±.5%	44	2.0±1.7%	1.0±.7%	50	0.73±.2%	0.42±.1%	58
Organic S	1.7±.5%	1.7±.5%	98	1.0±.74%	1±.7%	100	0.45±.1%	0.42±.1%	93
Be	1.5±.8	0.04±.03	3	0.70±.2	0.05±.03	7	0.40±.1	0.03±.03	8
B	148±81	8.1±2	5	53±42	14±7	26	59±33	7.3±6	12
Sc	29±.8	0.4±.3	1	4.9±2	1.2±0.9	24	1.4±.4	0.29±.2	21
V	37±17	6.5±4	18	48±22	9.3±13	19	17±12	2.3±2	14
Cr	28±13	5.7±3	20	20±7	7.3±4	36	2.7±3	1.1±.3	14
Co	5.3±3	0.4±.2	8	6.8±6	3.5±4	51	1.3±0.8	0.5±0.5	38
Ni	21±8	6.0±5	28	12±3	2.8±2	23	4.2±2	—	—
Cu	20±9	5.0±3	25	22±8	3.8±2	17	14±8	3.6±3	26
Zn	832±1700	<5	—	29±45	<1	—	10±9	—	—
Ga	3.2±1	0.60±.1	19	4.7±2	1.2±0.6	26	2.7±2	0.73±.8	27
As	6.8±8	<1	—	10±8	<1	—	1.8±2	0.5±.3	28
Se	2.6±.9	0.34±.2	13	3.1±2	0.58±.2	19	1.4±.4	0.39±.2	28
Br	8.9±7	6.0±4	67	11±9	6.7±6	61	1.1±.4	1.8±2	163
Rb	16.8±7	<1	—	14±4	—	—	1.8±.9	—	—
Sr	31±11	4.1±3	13	121±53	29±19	24	185±66	—	—
Mo	6.8±4	0.90±0.6	13	6±5	—	—	3.7±3	—	—
Cd	—	—	—	—	—	—	—	—	—
Sb	1.1±1	0.4±.3	30	2.3±2	0.40±.3	17	1.1±1	0.38±.2	34
Cs	1.3±.7	0.04±.03	3	1.4±.6	0.08±.08	6	0.19±.2	—	—
Ba	237±445	3.3±1.5	1	146±61	20±9	13	498±175	13±14	3
La	6.8±2	0.7±.2	3	13±6	2.8±1.2	22	5.7±2	1.3±.7	23
Ce	14.7±8	1.1±.4	36	21±8	3.2±.7	15	9.7±3	1.7±1	18
Sm	1.1±.4	0.30±.01	0.30±.1	2.2±.8	0.54±.3	24	0.69±0.2	0.21±.1	30
Eu	0.30±.1	0.06±.03	2	0.4±.2	0.12±.05	30	0.17±.07	0.05±.02	29
Tb	0.26±.1	—	—	0.02±.09	—	—	0.15±.04	—	—
Dy	1.0±.4	0.26±.1	26	1.7±0.7	—	—	0.60±0.2	—	—
Yb	0.58±.2	0.13±.06	22	0.58±.2	0.19±.04	33	0.39±.2	0.11±.04	28
Lu	0.09±.02	0.03±.01	33	0.13±.08	0.06±.03	46	0.07±.02	0.02±.01	28
Hf	0.70±.3	0.09±.04	13	1.3±.4	0.29±.2	22	0.99±.2	0.26±.1	26
Ta	0.17±.07	—	—	0.37±.3	0.09±.01	24	0.13±.05	—	—
W	0.68±.4	—	—	0.57±.4	0.26±.3	46	0.80±.3	—	—
Pb	29±27	—	—	8.9±9	—	—	4.1±1	—	—
Th	2.1±0.8	0.52±.2	25	4.1±2	1.0±.4	23	2.0±.9	0.80±.2	40
U	2.3±2	0.22±.1	10	1.2±1	0.27±.2	22	0.98±0.2	0.13±.1	13
ISA†	197	—	—	—	—	—	—	—	—

*All values in ppm unless noted. Less than values were not included in calculation of means.
†Internal surface area by CO₂ method (values in m²/g).

TABLE 8. Identification of coal samples and gravity separations*

<u>Analysis number</u>	<u>State</u>	<u>Coal seam</u>	<u>Specific gravity fraction</u>	<u>Percentage of raw coal</u>
<u>Float-sink set No. 1</u>				
C18560	Illinois	Herrin (No. 6)	RAW	
C18562			28M x 0	
C18563			1.29F	34.3
C18564			1.33FS	25.9
C18565			1.40FS	18.6
C18566			1.60FS	12.5
C18567			1.6S	8.7
<u>Float-sink set No. 2</u>				
C17001	Illinois	Davis	RAW	
C18090			3/8 x 28M	
C18094			1.28F	25.9
C18095			1.30FS	19.5
C18096			1.32FS	19.7
C18097			1.40FS	19.3
C18098			1.60FS	7.2
C18099			1.60S	8.5
<u>Float-sink set No. 3</u>				
C16137	Illinois	Herrin (No. 6)	RAW	
C18121			3/8 x 28M	
C18122			28M x 0	
C18123			1.25F	36.1
C18124			1.29FS	17.4
C18125			1.33FS	14.7
C18126			1.40FS	9.3
C18127			1.60FS	6.9
C18128			1.60S	15.6
<u>Float-sink set No. 4</u>				
C18841	West Virginia	Pittsburgh No. 8	RAW	
C18892			3/8 x 28M	
C18893			1.28F	33.8
C18894			1.30FS	20.9
C18895			1.40FS	25.7
C18896			1.60FS	13.5
C18897			1.60S	6.1
<u>Float-sink set No. 5</u>				
C19824	West Virginia	Pittsburgh No. 8	RAW	
C19827			1.28F	27.8
C19828			1.29FS	26.5
C19829			1.32FS	19.7
C19830			1.40FS	13.3
C19831			1.60FS	5.5
C19832			1.60S	7.2

TABLE 8. (Continued)

Analysis number	State	Coal seam	Specific gravity fraction	Percentage of raw coal
<u>Float-sink set No. 6</u>				
C18820	West Virginia	Pocohontas No. 4	RAW	
C18890			3/8 x 28M	
C18891			28M x 0	
C18883			1.30F	24.7
C18884			1.33FS	25.3
C18885			1.40FS	25.0
C18886			1.59FS	14.1
C18887		1.59S	10.9	
<u>Float-sink set No. 7</u>				
C18848	Alabama	Blue Creek	RAW	
C18889			28M x 0	
C18878			1.30F	25.3
C18879			1.32FS	20.5
C18880			1.40FS	36.0
C18881			1.60FS	11.8
C18882			1.60S	6.4
<u>Float-sink set No. 8</u>				
C19854	Montana	Rosebud	RAW	
C19848			1.301F	36.8
C19849			1.32FS	24.4
C19850			1.32FS	13.1
C19851			1.40FS	12.3
C19852			1.60FS	10.4
C19853			1.60S	3.0
<u>Float-sink set No. 9</u>				
C19000	Arizona	Black Mesa Field	RAW	
C19014			28M x 0	
C19009			1.28	25.0
C19010			1.30FS	26.3
C19011			1.40FS	40.8
C19012			1.60FS	6.9
C19013			1.60S	1.0

*For analytical results of concentrations of major, minor, and trace elements in the coal fractions, see Gluskoter et al., 1977, p. 90-104, and Kuhn et al., 1978, p. 5-8.

TABLE 9. Concentrations and organic affinities of elements for sample C18560 from Herrin (No. 6) Coal Member in Illinois

Element	Organic affinity	Organic fractions					
		Raw coal		F/S ext*		MMF†	
		(%)	(ppm)	(%)	(ppm)	(%)	(ppm)
Al	.30	1.40		0.10			41
Ca	.06	0.51		0			25
Fe	.06	2.60		0			66
K	.56	0.13		0.04			<1
Mg	.27	0.06		0.003			21
Na	.64	0.04		0.01			6
Ti	.29	0.06		0.13			20
Si	.45	3.20		0.017			41
Organic S	1.11	1.87		2.33		1.81	
Total S	.45	6.45		1.1		1.81	
As	.04		3.4		0		<.7
B	.77		200		57		6.6
Ba	.15		54		2		<2
Be	.87		1.4		0.6		0.03
Br	.92		13.4		12		3.3
Cd	.07		<0.1		0		<0.1
Ce	.07		25		0		1.7
Co	.74		7.2		1.7		.4
Cr	.77		21		20		7
Cs	.44		2.0		0.2		0.1
Cu	.66		13		3.3		2.1
Dy	.89		1.2		0.8		0.4
Eu	.67		.3		0.1		0.1
Ga	.15		2.4		0.3		.7
Hf	.48		1.1		0.1		0.1
La	.04		6.1		0		0.7
Lu	.59		0.1		0.03		<.01
Mn	.06		60		0		0.3
Ni	.75		24		5.9		<1
P	.03		50		0		<1
Pb	.32		<1.0		0.3		<1
Rb	.45		23		0.3		<1
Sb	.90		0.5		0.4		.1
Sc	.57		4.1		0.8		0.6
Se	.28		4.3		0		.3
Sm	.39		0.9		0.2		0.4
Sr	.07		33		0.8		1.5
Ta	.44		0.2		0.05		0.1
Th	.55		3.6		0.8		1.0
U	1.29		1.9		2.7		0.1
V	.97		36		35		3.5
W	---		0.6		---		0.1
Yb	.52		0.8		0.2		0.2
Zn	.04		57		0		1

*Extrapolation of float-sink data.

†Concentration in the acid demineralized residue of the 1.40 float fraction of the coal.

TABLE 10. Concentrations and organic affinities of elements for sample C17001 from Davis Coal Member in Illinois

Element	Organic affinity	Organic fractions					
		Raw coal		F/S ext*		MMF†	
		(%)	(ppm)	(%)	(ppm)	(%)	(ppm)
Al	.58	0.86		.32			125
Ca	.63	0.82		.16			67
Fe	.04	2.76		0			64
K	.63	0.14		.05			31
Mg	.41	0.02		.01			95
Na	.76	0.048		.009			25
Si	.50	2.08		.54			197
Ti	.76	0.06		.03			19
Organic S	1.09	1.51		1.2		1.57	
Total S	.10	4.14		0.1		1.57	
As	.05		9.4		0		<5
B	1.05		37		30		6.1
Be	1.03		1.6		2.7		0.1
Cd	.07		1.3		0		<0.1
Co	.65		8.0		1.3		<1
Cr	.69		30		5.5		<5
Cu	.56		8.0		2.7		1.8
Ga	.67		2.0		1.0		0.9
Mn	.35		22		3.9		0.7
Ni	.82		17		5.8		<4
P	.75		48		11		2.8
Pb	.04		56		0		<1
Sb	.68		2.5		0.2		0.6
Se	.69		3.3		1.3		<.5
V	.60		62		11.8		1.6
Zn	.02		170		0		<1

*Extrapolation of float-sink data.

†Concentration in the acid demineralized residue of the 1.40 float fraction of the coal.

TABLE 11. Concentrations and organic affinities of elements for sample C16137 from Herrin (No. 6) Coal Member in Illinois

Element	Organic affinity	Organic fractions					
		Raw coal		F/S ext*		MMF†	
		(%)	(ppm)	(%)	(ppm)	(%)	(ppm)
Al	.10	1.12		0			60
Ca	.04	0.73		0			13
Fe	.16	1.70		0.12			55
K	.13	0.18		0.004			1.3
Mg	.32	0.05			17		43
Na	43	0.02			140		6.6
Si	.09	2.48		0			36
Ti	.16	0.07		0.005			20
Organic S	1.15	1.95		1.58		1.12	
Total S	.54	3.25		1.56		1.12	
As	.05		27		0		<.5
B	.94		100		86		6.6
Be	.88		2.8		2.0		0.03
Cd	.04		---		0		0.1
Co	.35		8.0		1.1		0.2
Cr	.37		28		4.3		5.2
Cu	.26		20		2.1		4.1
Ga	.41		4.2		1.1		0.7
Mo	.52		9.0		.4		<1
Mn	.04		71		0		.3
Ni	.36		30		5.2		<3
P	.16		21		0		1.4
Pb	.05		72		0		<1
Sb	.67		4.2		1.0		0.6
Se	.39		2.4		0.7		0.4
V	.58		32		13		8.5
Zn	.04		2700		0		3

*Extrapolation of float-sink data.

†Concentration in the acid demineralized residue of the 1.40 float fraction of the coal.

TABLE 12. Concentrations and organic affinities of elements for sample C18841 from Pittsburgh (No. 8) seam in West Virginia

Element	Organic affinity	Organic fractions				
		Raw coal		F/S ext*		MMF†
		(%)	(ppm)	(%)	(ppm)	(%) (ppm)
Al	.34	1.20		0.14		280
Ca	.50	0.53		.10		210
Fe	.30	1.70		0		240
K	.12	0.19		0		0.7
Mg	.49	0.04		.011		7
Na	.54	0.060		.016		6
Si	.12	2.30		0		64
Ti	.05	0.06		0		94
Organic S	1.07	2.51		2.6		2.28
Total S	.71	5.02		2.4		2.28
As	.25		3.2		0	<.5
B	.81		120		45	24
Ba	.72		72		35	10
Be	.53		0.7		0.2	.01
Br	1.00		10		6.8	3.8
Cd	.66		<.1		.1	<0.1
Ce	.41		15		1.2	3.3
Co	.53		3.3		0.6	0.8
Cr	.40		15		3.2	8.6
Cs	.09		1.0		0	0.03
Cu	.47		5.1		1.3	<0.3
Dy	.65		1.5		0.5	---
Eu	.54		0.3		0.1	.1
Ga	.53		4.3		1.0	1.7
Hf	.30		0.7		0.1	.1
La	.45		8.7		1.7	2.4
Lu	.26		.1			0.05
Mn	.43		20		5.6	3.7
Ni	.44		6.3		1.4	3
P	.71		59		28	2
Pb	.62		3.0		1.5	<1
Rb	.20		13		.8	<1
Sb	.41		0.2		0.02	0.1
Sc	.40		2.6		0.3	1.3
Se	.36		1.1		0.04	0.4
Sm	.44		1.5		0.21	0.6
Sr	1.03		110		66	---
Ta	.24		0.8			<.01
Tb	.33		0.1		0.02	<.07
Th	.23		2.9		0.04	0.6
U	.79		0.7		0.4	0.1
V	.48		26		5.0	4
Yb	.32		0.4		0.01	0.2
Zn	.42		14		1.5	1.0

*Extrapolation of float-sink data.

†Concentration in the acid demineralized residue of the 1.40 float fraction of the coal.

TABLE 13. Concentrations and organic affinities of elements for sample C19824 from Pittsburgh (No. 8) seam in West Virginia

Element	Organic affinity	Organic fractions					
		Raw coal		F/S ext*		MMF†	
		(%)	(ppm)	(%)	(ppm)	(%)	(ppm)
Al	.62	1.02		0.43			41
Ca	.04	1.61		0			30
Fe	.17	1.12		0			80
K	.10	0.102		0			2.5
Mg	.04	0.16		0			<20
Na	.71	0.068		0.036			8.8
Si	.39	1.95		0.33			40
Ti	.58	0.06		0.023			11
Organic S	1.15	1.10		1.67		1.18	
Total S	.81	2.23		1.65		1.18	
As	.11		3.9		0		.3
B	1.14		82		86		---
Ba	.90		130		100		27
Be	.77		0.4		0.3		0.1
Br	1.02		12		12		12
Cd	.09		0.2		0		<.1
Ce	.68		16		6.2		2.5
Co	.79		2.2		1.5		0.2
Cr	.58		14		5.0		2.0
Cs	.28		0.8		0.1		0.03
Cu	.49		8.6		2.1		1.5
Dy	.67		0.8		0.4		0.5
Eu	.67		0.2		0.1		0.1
Ga	.79		2.6		2.1		1.4
Hf	.40		1.0		0.2		0.6
La	.68		5.7		3.0		2.6
Lu	.62		.1		0.03		0.02
Mn	.06		35		0		0.7
Mo	.04		1.7		0		<0.2
Ni	.62		9.0		2.6		2
P	.68		103		42		<5
Pb	.04		25		0		<1
Rb	.18		9.5		0		<1
Sb	.37		1.6		0.2		0.8
Sc	.67		2.3		1.1		0.1
Se	.53		1.6		0.7		0.5
Sm	.72		0.9		0.5		0.5
Sr	.94		143		0.1		24
Ta	.51		.2		0.04		0.1
Tb	.90		0.1		0.1		0.04
Th	.62		2.1		0.7		1.1
U	.74		0.6		0.7		0.1
V	.57		17		6.6		2.7
W	.67		0.3		0.2		<0.9
Yb	.74		0.3		0.2		0.1
Zn	.31		10.3		0.8		1

*Extrapolation of float-sink data.

†Concentration in the acid-demineralized residue of the 1.40 float fraction of the coal.

TABLE 14. Concentrations and organic affinities of elements for sample C18820 from Pocahontas (No. 4) seam in West Virginia

Element	Organic affinity	Organic fractions					
		Raw coal		F/S ext*		MMF†	
		(%)	(ppm)	(%)	(ppm)	(%)	(ppm)
Al	.25	1.40		0.15			169
Ca	.53	0.56		0.15			74
Fe	.67	0.90		0.43			72
K	.12	0.21		0			<10
Mg	.37	0.06		0.011			18
Na	.50	0.070		0.012			0.5
Si	.11	2.50		0			56
Ti	.29	0.12		0.021			19
Organic S	1.18	0.51		0.58		0.47	
Total S	.82	0.80		0.56		0.47	
As	.07		15		0		<0.5
B	.47		8		2.1		9.7
Ba	.77		220		120		33
Be	.87		0.1		0.9		0.1
Br	1.07		22		28		16
Cd	.63		0.1		0.1		<0.1
Ce	.50		33		9.4		4.5
Co	1.16		7.0		6.7		5.4
Cr	.38		17		3.2		6.3
Cs	.14		1.9		0		0.2
Cu	.55		20		8.3		6.5
Dy	.60		2.0		0.9		0.9
Eu	.57		0.5		0.2		0.2
Ga	.49		4.0		1.5		0.7
Hf	.24		1.3		0.1		0.2
La	.41		20		4.9		5.0
Lu	.52		0.1		0.04		0.05
Mn	.40		14		3.8		0.5
Ni	.99		12		11		<5
P	.65		26		16		0.1
Pb	.38		1.6		1.1		<1
Rb	.12		16		0		<1
Sb	.55		4.6		0.4		.6
Sc	.48		3.0		0.9		2.0
Se	.46		5.8		1.6		1
Sm	.46		2.7		0.7		0.9
Sr	.89		120		78		50
Ta	.28		0.1		0.03		0.1
Tb	.54		0.3		0.1		<1
Th	.29		5.9		0.5		1.1
U	.40		1.1		0.3		0.2
V	.56		22		15		1.5
W	.80		0.5		0.5		0.1
Yb	.60		0.7		0.3		.2
Zn	.52		11		2.2		<1

*Extrapolation of float-sink data.

†Concentration in the acid demineralized residue of the 1.40 float fraction of the coal.

TABLE 15. Concentrations and organic affinities of elements for sample C18848 from Blue Creek seam in Alabama

Element	Organic affinity	Organic fractions					
		Raw coal		F/S ext*		MMF†	
		(%)	(ppm)	(%)	(ppm)	(%)	(ppm)
Al	.40	1.90		0.25			240
Ca	.34	0.35		0.037			48
Fe	.44	0.70		0.14			54
K	.12	0.28		0			2.3
Mg	.07	0.05		0			<20
Na	.20	0.030		0			<3
Si	.17	2.80		0			64
Ti	.54	0.15		0.04			28
Organic S	1.08	0.50		0.53		0.33	
Total S	1.08	0.55		0.56		0.36	
As	.05		1.8		0		<0.5
B	.37		15		0.8		5.1
Ba	.62		230		76		20
Be	.76		0.7		0.4		0.05
Br	1.20		2.5		2.5		1.7
Cd	.45		<0.1		0.05		<0.1
Ce	.64		30		14		3.5
Co	1.08		9.4		7.9		10
Cr	.60		21		7.1		14
Cs	.10		2.3		0		0.05
Cu	.78		12		8.0		4.1
Dy	.78		2.1		1.5		.7
Eu	.78		0.4		0.2		0.1
Ga	.64		6.3		2.6		1.7
Hf	.44		1.2		0.3		0.3
La	.74		18		9.6		2.8
Lu	.69		0.1		0.04		0.1
Mn	.05		13		0		<1
Ni	1.01		11		9.9		1
P	.60		190		90		<4
Pb	.68		12		1.9		<1
Rb	.10		18		0		<1
Sb	.64		0.8		0.2		0.7
Sc	.53		4.3		1.2		2.5
Se	.58		3.0		0.9		.4
Sm	.66		2.8		1.0		0.1
Sr	.80		130		54		13
Ta	.34		1.1		0.04		<0.1
Tb	.66		0.2		0.2		<.1
Th	.43		5.4		0.6		5
U	.71		0.9		0.8		0.3
V	.75		54		29		<5
W	.70		0.4		0.3		0.1
Yb	.56		0.9		0.2		.2
Zn	.21		2.0		0		<1

*Extrapolation of float-sink data.

†Concentration in the acid demineralized residue of the 1.40 float fraction of the coal.

TABLE 16. Concentrations and organic affinities of elements for sample C19854 from Rosebud seam in Montana

Element	Organic affinity*	Raw Coal		Organic fractions			
		(%)	(ppm)	F/S Ext [†]		MMF [‡]	
		(%)	(ppm)	(%)	(ppm)	(%)	(ppm)
Al	.18	1.15		0			20
Ca	.82	0.97		0.43			20
Fe	.02	0.47		0			35
K	.02	0.079		0			<5
Mg	.97	0.44		0.32			<20
Na	.88	0.019		0.009			15
Ti	.15	0.05		0			4
Si	.06	2.41		0			30
Organic S	1.10	0.62		0.53		0.56	
Total S	.74	.90		0.59		0.46	
As	.03		0.7		0		<.3
B	1.24		100		115		--
Ba	.02		808		0		40
Be	.73		0.5		0.1		0.03
Br	.99		1.6		5.0		4.5
Cd	.06		0.2		0		<0.1
Ce	.89		10.3		5.3		3.3
Co	.80		1.2		0.6		1.5
Cr	.09		6.2		0		0.6
Cs	.03		0.4		0		<0.04
Cu	.44		8.8		1.2		1.8
Dy	.77		0.6		0.3		0.2
Eu	.89		--		0.1		0.04
Ga	.76		3.3		1.7		2.2
Hf	.39		1.2		0.2		0.2
La	.90		5.2		3.1		1.3
Lu	.68		0.1		0.02		0.03
Mn	.04		85		0		1.5
Mo	.83		7.1		2.6		1.4
Ni	.64		3.1		0.8		<2
P	1.02		121		95		<5
Pb	.04		4.6		0		<1
Rb	.03		3.3		0		<1
Sb	.95		--		0.5		0.7
Sc	.78		1.6		0.7		0.6
Se	.05		0.9		0		0.3
Sm	.73		0.9		0.3		0.2
Sr	.98		103		94		4.4
Ta	.61		0.1		0.5		.1
Tb	.79		0.1		0.5		0.05
Th	.56		2.5		0.6		.8
U	.58		1.5		0.2		0.2
V	.60		10.6		2.3		1.2
W	1.15		0.7		.7		<.1
Yb	.74		0.2		.1		0.2
Zn	.02		4.3		0		<0.3

*Organic affinity calculated on unadjusted washability curve.

[†]Extrapolation of float-sink data.

[‡]Concentration in the acid demineralized residue of the 1.40 float fraction of the coal.

TABLE 17. Concentrations and organic affinities of elements for sample C19000 from Black Mesa Field in Arizona.

Element	Organic affinity	Organic fractions					
		Raw coal		F/S Ext*		MMF†	
		(%)	(ppm)	(%)	(ppm)	(%)	(ppm)
Al	.39	1.40		0.12			187
Ca	.82	0.46		0.65			200
Fe	.89	0.40		0.28			225
K	.53	0.02		0.007			<10
Mg	.95	0.07		0.064			<20
Na	1.00	0.150		0.153			1.4
Ti	.33	0.06		0.007			54
Si	.10	0.71		0			53
Organic S	.95	0.52		0.41		0.32	
Total S	.88	0.72		0.32		0.32	
As	.11		1.0		0		0.2
B	1.09		37		37		5.3
Ba	.92		270		220		15
Be	.79		0.4		0.4		0.03
Br	.83		0.9		1.3		1.0
Cd	.99		<0.1		0.1		<0.1
Ce	.64		6.0		4.6		1.2
Co	.83		0.8		0.6		0.5
Cr	.54		3.5		1.3		1.4
Cs	.03		0.1		0		<0.05
Cu	.74		4.7		2.4		<3
Dy	.82		0.6		0.5		--
Eu	.57		0.2		0.05		0.05
Ga	.38		2.3		0.4		0.2
Hf	.47		0.6		0.3		0.2
La	.58		6.0		2.1		1.3
Lu	.72		0.1		0.04		0.03
Mn	.53		1.4		1.1		0.4
Ni	.88		1.5		1.2		<1.5
P	.94		120		96		<4
Pb	.06		<.7		0		<1
Rb	.40		1.2		0.3		<1
Sb	.66		0.4		0.1		.2
Sc	.64		1.3		0.7		0.4
Se	.61		1.6		0.7		0.6
Sm	.47		0.8		0.2		.3
Sr	.84		200		130		--
Ta	.39		0.1		0.03		--
Tb	.54		0.1		0.05		<.05
Th	.38		1.4		0.4		0.6
U	.50		<0.7		0.4		0.05
V	.74		7.1		8.7		<5
W	.52		1.2		0.1		<.3
Yb	.75		0.2		0.2		.1
Zn	2.2		7.0		2.3		<0.5

*Extrapolation of float-sink data.

†Concentration in the acid demineralized residue of the 1.40 float fraction of the coal.

The extrapolated values are thought to represent the theoretical concentration of an element in a coal when no mineral matter is present or, in other words, the quantity of an element that is intimately associated with the organic matrix.

EXCHANGEABLE AND SOLUBLE IONS

Results of analyses of raw coals and their residues, which have been leached with ammonium acetate, are given in table 18. Comparison of the two values (raw coal minus residue) is a good indicator of the potential for removal of exchangeable ions and soluble elements from coal. However, the data may be subject to some error when comparisons are made for interpretive purposes with data in tables 9-17 because different samples of the same coals were used in the two studies. The desirability of making this comparison is discussed in the section on "Validity of Organically Associated Elements," page 50.

MINERALOGY

The results of qualitative mineral analyses for 26 whole coals in this study are presented in table 19. Certain mineral phases, such as kaolinite, illite, expandable clays, calcite, pyrite, and quartz, are ubiquitous in these coals. However, some regional differences in mineralogy related to depositional and geochemical environments can be observed and are in agreement with the findings of previous workers (Rao and Gluskoter, 1973; O'Gorman and Walker, 1972; Miller and Given, 1978).

As a group, the western United States coals in this study have distinctively different mineral assemblages from the other two regions. Bassanite composes a major mineral phase in the low temperature ash of western lignites and subbituminous coals; it forms during the low temperature ashing process both by the dehydration of the mineral gypsum, when it is present, and by the fixation of exchangeable calcium cations, which are common in low rank coal containing organic sulfur (Miller and Given, 1978). The exception in the group is a high volatile bituminous coal from Arizona in which the level of exchangeable cations is quite low. Another major difference between western United States coals and the other two groups studied is the predominance of very high intensity, well-crystallized kaolinite over other clay minerals in the LTA. There are traces of barite, chlorite, and aragonite in these coals.

Eastern United States and Illinois Basin coals are somewhat similar mineralogically, although a higher frequency of iron carbonate minerals is evident in the eastern coals studied. Pyrite content is likely to be highly variable throughout both regions. The presence of the iron sulfates, szomolnokite and coquimbite, in these samples is primarily due to the oxidation of pyrite during storage, although it is possible that limited quantities of these sulfates can be produced in the low temperature asher. Detectable amounts of epigenetic sphalerite are characteristic of northwestern Illinois coals.

Nine of the 27 coals (see table 8) were studied in greater detail to evaluate the distribution of the major mineral phases in the various specific gravity fractions of each coal. Quantitative x-ray diffraction determinations

TABLE 18. Comparison of concentrations of minor and trace elements in coal and NH₄AC extracted residue

	C18126		C18841		C18848		C19000		C19824		C19854		C18440	
	Raw coal	Leached residue	Raw coal	Leached residue	Raw coal	Leached residue	Raw coal	Leached residue	Raw coal	Leached residue	Raw coal	Leached residue	Raw coal	Leached residue
Si (%)	1.17	1.15	1.22	1.21	1.72	1.71	.75	.64	2.17	2.27	2.30	2.31	.88	.90
Al (%)	.73	.69	1.01	.95	1.44	1.45	.54	.55	1.30	1.31	1.35	1.37	.85	.76
Fe (%)	.74	.76	1.3	1.1	.15	.15	.18	.18	1.2	1.1	.41	.47	.31	.33
Ca (%)	.08	.07	.20	.12	.11	.06	.80	.51	1.21	1.02	0.97	0.26	2.33	0.85
Na (ppm)	240	75	312	180	170	136	1520	62	715	594	208	107	3640	56
Mg (%)	.03	.02	.03	.02	.02	.02	.07	.04	.07	.04	.23	.06	.26	.05
K (%)	0.10	0.10	.08	.08	.16	.16	.009	.009	.13	.14	.09	.09	.06	.04
Ti (%)	.06	.06	.04	.04	.04	.04	.05	.05	.07	.18	.06	.07	.02	.02
P (ppm)	14	13	48	51	190	204	170	160	118	106	117	124	236	171
Mn (ppm)	10	6.5	12	10	5.3	4.6	---	---	32	36	105	74	59	43
S (%)	3.3	3.3	5.0	4.8	.92	.92	.84	.86	2.29	2.32	.81	.83	.67	.69
Cl (%)	.22	.02	.02	.01	.02	.01	.12	.07	.14	.09	.02	.01	.02	.01
As (ppm)	2.0	1.9	2.5	2.1	.5	.2	0.6	0.8	4.9	5.0	1.4	1.1	2.1	2.4
Ba (ppm)	80	70	32	28	154	135	242	225	120	110	800	700	500	400
Be (ppm)	2.8	2.7	0.7	0.7	0.7	0.7	0.4	0.4	.3	.3	.5	.5	.5	.5
Br (ppm)	12.5	5.6	6.0	4.2	3.2	2.6	2.6	1.6	10.5	9.3	.6	.4	3.1	1.4
Ce (ppm)	3.5	4.3	8.0	6.5	22	22	5.5	5.6	11	10	8.3	9.5	8.3	8.0
Co (ppm)	2.5	2.1	2.1	1.6	8.5	8.2	0.9	0.7	2.1	2.1	1.1	1.3	1.0	.9
Cr (ppm)	17.2	17.9	9.8	8.5	17	16	2.8	2.9	16	17	6.0	6.0	3.2	3.4
Cs (ppm)	2.5	0.6	0.3	0.3	0.7	0.7	---	---	7	5	3	3	.14	.13
Cu (ppm)	21	23	5.1	5.0	12	12	4.7	5.3	8.6	8.2	8.8	9.1	2.8	2.7
Dy (ppm)	0.6	0.6	0.6	0.6	1.2	1.2	0.5	0.5	.7	.2	.6	.5	.3	.5
Eu (ppm)	0.09	0.09	0.15	0.14	0.4	0.3	.11	.11	.2	.2	.12	.13	.11	.10
Ga (ppm)	3.3	3.0	2.8	2.6	4.0	4.2	1.3	1.3	2.8	2.7	3.0	3.8	2.3	2.3
Hf (ppm)	0.4	0.5	0.3	0.3	0.8	0.8	.6	.5	.7	.6	.9	1.0	.8	.8
La (ppm)	2.1	2.3	3.8	3.8	11.5	11.9	3.8	3.9	5.8	5.8	5.0	5.5	5.7	6.0
Lu (ppm)	0.06	0.10	.07	.05	0.11	0.11	.07	.05	.08	.07	.06	.07	.07	.05
Ni (ppm)	2.6	2.9	14	14	15	17	2.4	2.3	.9	9.4	3.4	1.5	4	1.5
Rb (ppm)	7.7	7.8	7	3	6	7	---	---	6.5	9	4.7	4.7	2.7	1.9
Sb (ppm)	1.4	1.6	.16	0.14	0.6	0.6	.2	.2	3.8	3.2	.6	.7	.9	.8
Sc (ppm)	2.5	2.7	1.8	1.6	3.7	3.7	1.2	1.1	2.1	2.1	1.4	1.5	1.1	1.2
Se (ppm)	2.0	1.7	0.9	0.8	2.0	1.1	1.4	1.3	1.4	1.3	.8	.8	.7	.7
Sm (ppm)	0.5	0.4	0.7	0.7	1.6	1.7	.5	.5	.8	.8	.6	.8	.4	.5
Sr (ppm)	19	18	105	32	122	120	204	200	130	130	103	50	240	100
Ta (ppm)	.12	.11	.07	.07	.2	.2	.10	.9	.17	.12	.17	.15	.12	.13
Tb (ppm)	.13	.14	.17	.13	.26	.30	.10	.16	.15	.15	.13	.13	.10	.09
Th (ppm)	1.4	1.6	1.1	1.0	2.9	2.9	1.2	1.2	1.8	1.7	2.1	2.4	1.6	1.6
U (ppm)	1.4	1.4	.8	.5	2.2	1.2	---	.7	1.1	.5	1.5	1.7	1.6	2.0
V (ppm)	29	28	18	18	52	53	7	8	17	16	10	10	6	6
W (ppm)	.2	.3	.5	.5	.5	.3	---	.3	.4	.2	.8	.9	1.3	1.5
Yb (ppm)	.3	.4	.3	.3	.7	.7	.3	.3	.4	.3	.3	.4	.3	.3
Zn (ppm)	11	11	12	14	13	13	3	4.6	11	11	7.4	5.8	14	20
Pb (ppm)	71	71	5	4	12	11	.7	.5	25	28	6	6	5	7

TABLE 19. Results of qualitative mineral analysis of low-temperature ashes.

	Kaolinite	Illite	Expandable clays	Chlorite	Muscovite	Calcite	Dolomite	Siderite	Ankerite	Aragonite	Pyrite	Marcasite	Sphalerite	Szomolnokite	Coquimbite	Barite	Gypsum	Bassanite	Quartz	Plagioclase	Orthoclase	Apatite
<u>Illinois Basin</u>																						
C-14684	X	X	X			X					X			X	X				X			
C-15999	X	X	X								X			X	X				X			
C-16543	X	X	X			X					X		X	X	X				X			
C-16993	X	X				X					X				X				X			
C-17001*	X	X	X			X					X				X				X			
C-18126*	X	X	X			X					X		X						X			
C-18304	X	X									X	X		X			X		X			
C-18320	X	X	X			X					X	X		X	X				X	X		
C-18368	X	X	X			X					X			X				X	X			
C-18560*	X	X	X			X					X	X		X	X				X	X		
C-18571	X	X	X			X					X	X		X					X			X
C-18704	X	X	X			X					X			X		X			X	X		
C-18748	X	X				X					X			X					X			
C-18857	X	X	X			X					X			X	X				X			
<u>Eastern United States</u>																						
C-18820*	X	X				X		X	X		X								X			
C-18824	X										X								X			
C-18841*	X	X	X			X					X								X			
C-18844	X	X	X			X		X			X								X	X		
C-18848*	X		X		X	X		X			X								X			X
C-19824*	X	X	X			X	X				X			X					X		X	
<u>Western United States</u>																						
C-18440	X	X		X		X									X	X		X	X	X		
C-18445	X			X							X					X		X	X			
C-18457	X		X			X				X	X							X	X			
C-18816	X		X								X							X	X			
C-19000*	X										X								X			
C-19854*	X	X	X	X		X					X					X		X	X			

*Quantitative mineral analysis of washed fractions of these coals are presented in subsequent tables.

of pyrite, calcite, quartz, and other major minerals present in the washed fractions are given in table 20. The relative percentages of pyrite, calcite, quartz, and most of the minor minerals in the LTA generally increase in the heavier washed fractions as the relative percentage of total clays in each fraction decreases. These trends are especially evident in coals having numerous mineralized bands and partings or in coals having heavy epigenetic mineralization in cleats and fractures. Minerals such as these are easily removed during normal coal cleaning operations. In sets of washed coals having an inverse mineral distribution in the LTA, for example, siderite and ankerite in set 6 and bassanite in set 8, the data indicate that these minerals are finely disseminated in the coal and that they are intimately associated with the macerals rather than being in cleat fillings.

Examples of washability curves prepared from the mineral data in table 20 are shown in figure 9 for the Herrin (No. 6) Coal. These curves demonstrate that a large portion of the pyrite and calcite in this coal can be concentrated and removed through physical cleaning methods; removal of quartz and clay minerals is less efficient than removal of heavier minerals. Mineral washability curves for the remaining washed coals display similar results. Yancey and Geer (1962) suggest that the retention of clay minerals in the lighter fractions is due to the buoyant effect of imbedded coal in shale particles. The aggregation of quartz and clay minerals in detrital mineral bands found in the coal typically produces similar washing characteristics for the two groups of minerals.

Results of clay mineral analysis of the $<2\ \mu\text{m}$ fraction of the low temperature ash for 2 sets of washed coals are given in table 21. Because of the inherent problems involved with clay mineral preparation and analysis, these data are given to indicate general trends and are not absolute. Both coals

were found to contain higher proportions of kaolinite in the lighter fractions and increased amounts of illite and expandable clays in the 1.60 fraction. These data show that a dual population of clay minerals may be present in the coal. Shale particles having a specific gravity approximating 2.3—derived from partings, joint fillings, and other rock materials mined with the coal—are concentrated in the heaviest fraction. This shale component contains an increased amount of expandable clays and lesser amounts of kaolinite. The clay minerals associated with the coal macerals in the lighter washed fractions may be principally composed of authigenic kaolinite and moderate amounts of illite and other clays. The apparent distribution of all the clay minerals present in the washed fractions may also be affected by the disintegration of shale particles and their suspension in the washing medium; subsequently, lighter gravity fractions may be

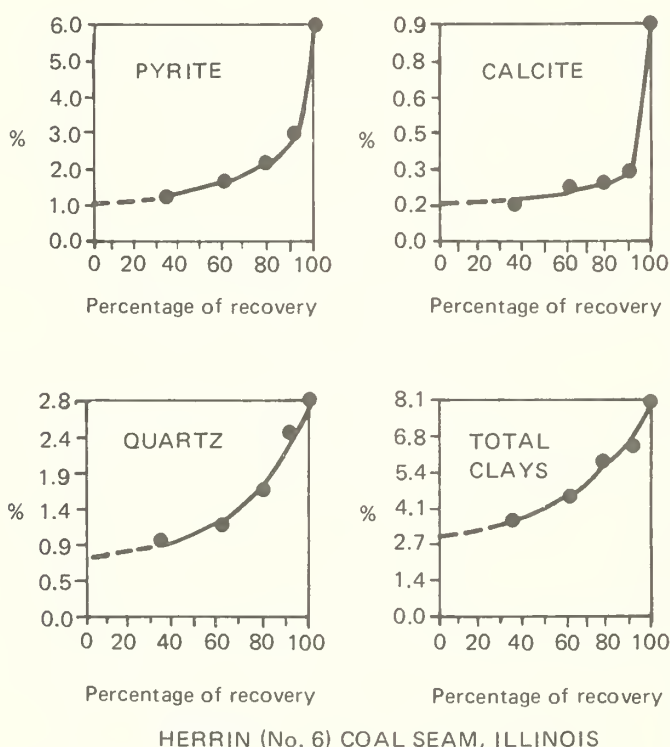


Figure 9. Mineral distributions in a single sample of the Herrin (No. 6) Coal Member, Illinois. (C18560)

TABLE 20. Results of mineralogical analysis

Average mineral percentages \pm 7.5% in low temperature ash (LTA)													
Sample No.	Fraction	Recovery (%)	LTA (%)	Pyrite (%)	Calcite (%)	Quartz (%)	Siderite (%)	Ankerite (%)	Bassanite (%)	Clays (%)			
Set 1													
C18560	Raw Coal	--	20.37	39	5	14	--	--	--	42			
C18562	28M x 0	--	25.17	28	6	14	--	--	--	51			
C18563	1.29F	34.3	6.10	19	3	16	--	--	--	62			
C18564	1.33FS	25.9	9.81	22	3	16	--	--	--	59			
C18565	1.40FS	18.6	17.62	23	2	18	--	--	--	57			
C18566	1.60FS	12.5	26.48	31	2	27	--	--	--	40			
C18567	1.60S	8.7	77.80	49	10	9	--	--	--	32			
Set 2													
C18090	3/8 x 28M	--	15.80	34	6	18	--	--	--	42			
C18094	1.28F	25.9	3.61	17	5	15	--	--	--	63			
C18095	1.30FS	19.5	5.56	15	5	17	--	--	--	63			
C18096	1.32FS	19.7	6.67	15	5	18	--	--	--	62			
C18097	1.40FS	19.3	12.74	16	7	20	--	--	--	57			
C18098	1.60FS	7.2	23.06	20	8	21	--	--	--	51			
C18099	1.60FS	8.5	73.53	65	2	7	--	--	--	26			
Set 3													
C18121	3/8 x 28M	--	26.28	15	5	14	--	--	--	66			
C18122	28M x 0	--	28.23	12	6	13	--	--	--	69			
C18123	1.25F	36.1	3.83	20	2	9	--	--	--	69			
C18124	1.29FS	17.4	5.01	21	2	16	--	--	--	61			
C18125	1.33FS	14.7	8.18	21	2	17	--	--	--	60			
C18126	1.40FS	9.3	14.86	22	2	15	--	--	--	61			
C18127	1.60FS	6.9	25.92	20	2	21	--	--	--	57			
C18128	1.60S	15.6	88.40	26	8	12	--	--	--	52			
Set 4													
C18841	Raw Coal	--	14.50				--	--	--				
C18892	3/8 x 28M	--	13.96	38	4	11	--	--	--	47			
C18893	28M x 0	--	15.38	36	5	12	--	--	--	47			
C18894	1.29F	33.8	3.89	29	7	6	--	--	--	58			
C18895	1.32FS	20.9	7.87	37	1	7	--	--	--	55			
C18896	1.40FS	25.7	11.87	55	1	10	--	--	--	34			
C18897	1.59FS	13.5	22.43	50	2	8	--	--	--	40			
C18898	1.59S	6.1	63.79	25	7	22	--	--	--	46			

TABLE 20. *Continued*

Sample No.	Fraction	Recovery (%)	LTA (%)	Pyrite (%)	Calcite (%)	Quartz (%)	Siderite (%)	Ankerite (%)	Bassanite (%)	Clays (%)
Set 5										
C19824	Raw Coal	--	14.49	16	22	8	--	--	--	54
C19827	1.275F	27.8	5.11	10	2	7	--	--	--	81
C19828	1.292F	26.5	6.42	13	3	7	--	--	--	77
C19829	1.32FS	19.7	9.28	18	2	6	--	--	--	74
C19830	1.40FS	13.3	14.01	21	3	9	--	--	--	67
C19831	1.60FS	5.5	24.14	30	7	14	--	--	--	49
C19832	1.60S	7.2	80.04	14	60	10	--	--	--	16
Set 6										
C18820	Raw Coal	--	12.90	3	3	6	4	3	--	81
C18890	2/8 x 28M	--	13.73	3	3	7	4	2	--	81
C18891	28M x 0	--	12.44	2	3	6	4	2	--	83
C18883	1.30F	24.7	1.93	2	2	3	9	2	--	82
C18884	1.33FS	25.3	3.39	3	2	2	8	3	--	82
C18885	1.40FS	25.0	7.75	3	2	7	4	6	--	78
C18886	1.59FS	14.1	20.50	3	2	18	1	4	--	72
C18887	1.59S	10.9	64.58	5	4	24	0	0	--	67
Set 7										
C18848	Raw Coal	--	12.67	<1	4	8	2	--	--	85
C18889	28M x 0	--	11.38	<1	4	10	3	--	--	82
C18878	1.30F	25.3	3.76	<1	4	4	1	--	--	90
C18879	1.32FS	20.5	6.15	<1	4	4	3	--	--	88
C18880	1.40FS	36.0 ^a	9.71	<1	4	9	3	--	--	83
C18881	1.60FS	11.8	19.76	<1	6	7	6	--	--	80
C18882	1.60S	6.4	59.75	<1	6	26	9	--	--	58
Set 8										
C19854	Raw Coal	--	13.09	3	4	13	--	--	--	64
C19848	1.301F	36.8	7.41	<1	<2	9	--	--	--	68
C19849	1.32FS	24.4	9.46	<1	<3	12	--	--	--	70
C19850	1.35FS	13.1	6.91	<1	<3	10	--	--	--	66
C19851	1.40FS	12.3	11.35	<1	<7	13	--	--	--	61
C19852	1.60FS	10.4	20.53	<1	10	20	--	--	--	60
C19853	1.60S	3.0	62.88	28	10	20	--	--	--	42
Set 9										
C19000	Raw Coal	--	8.75	1	9	22	--	--	--	68
C19014	28M x 0	--	9.20	1	10	21	--	--	--	68
C19009	1.28F	25.0	4.03	<1	<1	19	--	--	--	79
C19010	1.30FS	26.3	4.37	1	10	21	--	--	--	68
C19011	1.40FS	40.8	7.87	1	10	24	--	--	--	65
C19012	1.60FS	6.9	22.72	2	8	27	--	--	--	63
C19013	1.60S	1.0	79.67	2	6	29	--	--	--	63

TABLE 21. Results of clay mineral analysis (<2 μ m fraction of LTA) of two coals.

	Sample no.	Fraction	Illite (%)	Kaolinite (%)	Mixed layer clays (%)	Chlorite (%)
Pittsburgh (No. 8), West Virginia	C19824	Raw coal	26	47	27	—
	C19827	1.275F	20	60	20	—
	C19828	1.292FS	21	65	14	—
	C19829	1.32FS	21	62	17	—
	C19830	1.40FS	21	55	24	—
	C19831	1.60FS	25	38	37	—
	C19832	1.60S	33	19	48	—
Rosebud, Montana	C19854	Raw coal	17	64	11	8
	C19848	1.301F	17	68	5	10
	C19849	1.32FS	12	71	9	8
	C19850	1.35FS	16	77	7	—
	C19851	1.40FS	17	71	12	—
	C19852	1.60FS	20	67	13	—
	C19853	1.60S	28	56	16	—

contaminated. Although the effect would be much more pronounced in a water-based medium, it is not evident to what degree this type of contamination may be exhibited by the samples studied.

SECTION V

DISCUSSION

VALIDITY OF ORGANICALLY ASSOCIATED ELEMENTS

The two methods for determining organically associated elements (described in Section 3) yield values that are in substantial agreement for the estimation of many organically associated elements in coal. Usually, agreement is best where analytical values are higher and most reliable. The poorest agreement was obtained for B, V, P, Ba, Sr, and Be.

In the last two columns of tables 9 through 17, the values determined in the mineral-matter-free coal material may be compared with the values obtained by extrapolation of adjusted coal washability curves to 0 percent coal recovery. The relationship between these two sets of values for organic sulfur in 9 coals is summarized graphically in figure 10. Figures 11 through 14 are typical plots of trace-element concentrations (float/sink extrapolated vs. mineral-matter-free) in each of four coals. (For clarity not all elements determined have been plotted.) Figures 11-14 also contain a line for the case $X = Y$ (i.e., a one to one correspondence of concentrations) and lines for plus and minus 50 percent limits of $X = Y$.

For the most part, the two sets of values compare well; however, it is recognized that the demineralization procedure may alter coal microporosity (Majahan and Walker, 1979). Also, organic molecules, chelated elements, and exchangeable ions may be removed through oxidation or dissolution. (Exchangeable ions are also sometimes cited as being organically associated.) Despite the use of HNO_3 , which was used for the extraction of pyrite, the analytical data in table 3 and figure 10 show that very little organic sulfur is removed by the acid treatment; this suggests that the "coal molecule" itself has not been significantly altered. Furthermore, the favorable comparison between results of analyses of chemically-treated (MMF) coal and the results obtained by extrapolating data from float-sink washability studies, where removal of chelated elements is much less likely to occur, indicates that concentrations of chelated elements, if indeed they are such, are not altered sufficiently by acid extraction to be of major concern in most bituminous coals.

Nevertheless, some large variations in the two sets of data remain. For example, the extrapolated value for Na from adjusted float-sink data was 0.15 percent for C-19000 (table 17), and the concentration of Na in the mineral-matter-free material (MMF) was only 1.4 ppm. Major variations also exist in some coals for Ba, B, Ca, and Sr; but data in table 18 indicate that these elements are present in exchangeable or soluble form. An example of this effect is shown in figure 15 where the exchangeable and soluble Ca in Rosebud seam coal is approximately equal to the difference between the

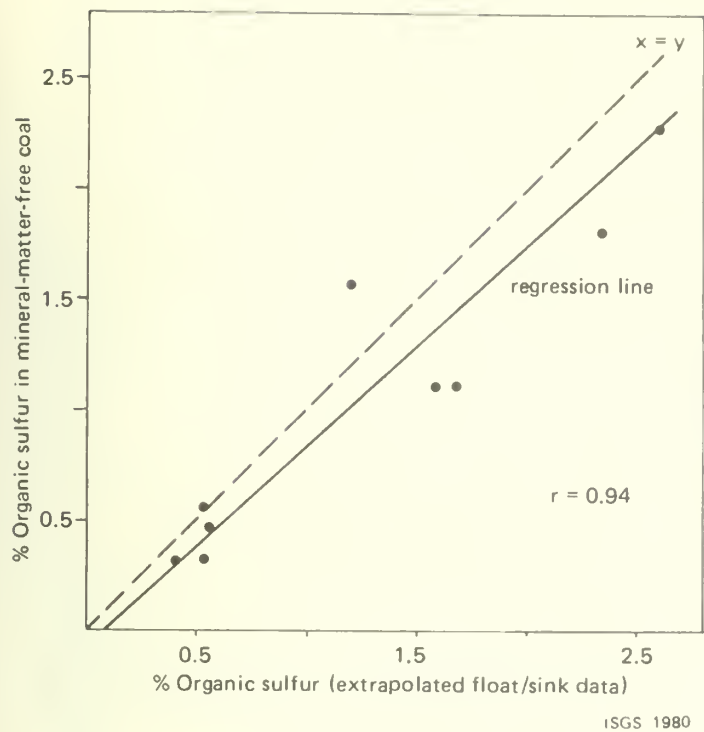


Figure 10. Comparison of independently determined concentrations of organic sulfur in nine coals.

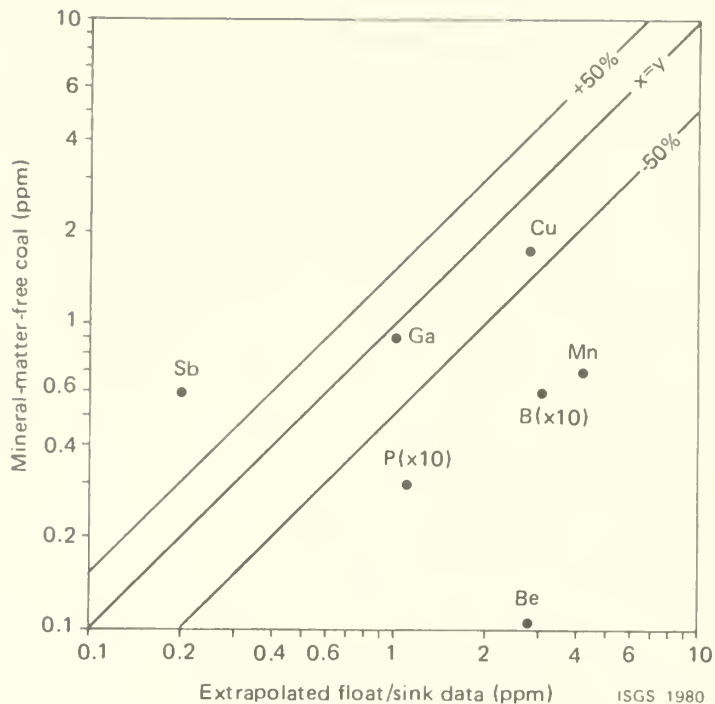


Figure 11. Comparison of independently determined concentrations of organically associated trace elements in the Davis Coal Member, Illinois (C17001).

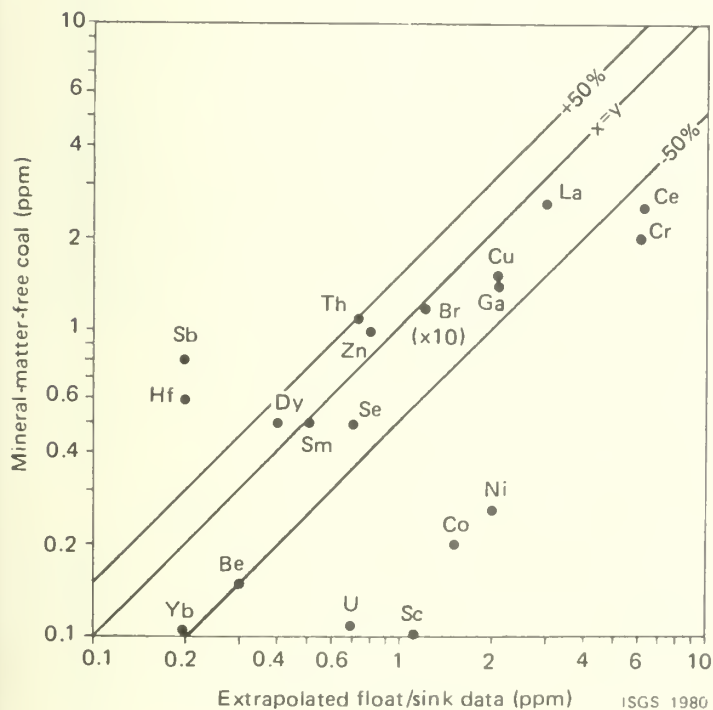


Figure 12. Comparison of independently determined concentrations of organically associated trace elements in the Pittsburgh No. 8 seam, West Virginia (C19824).

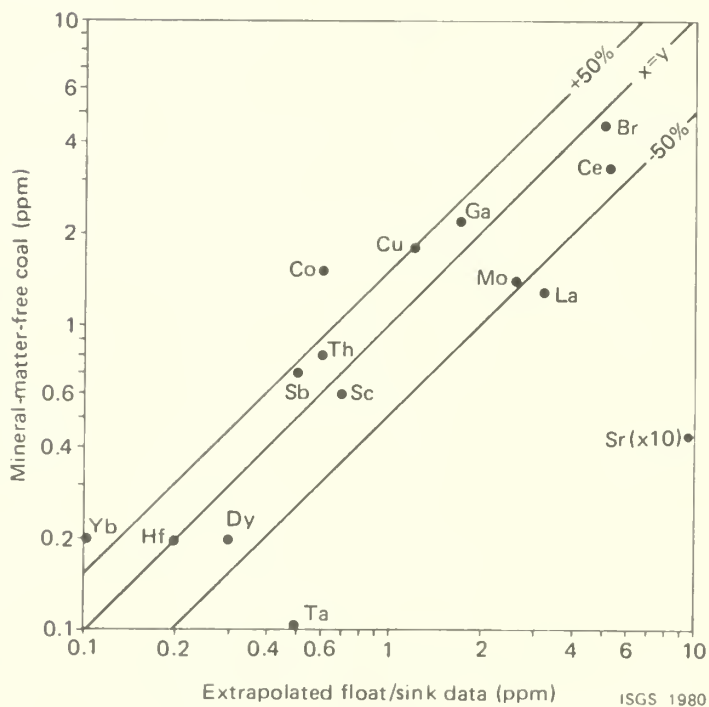


Figure 13. Comparison of independently determined concentrations of organically associated elements in the Rosebud Coal, Montana (C19854).

float-sink extrapolated and mineral-matter-free material values. (Strontium in figure 13 is probably another such example.) In the case of B (figs. 11 and 14), high concentrations from extrapolated float/sink data relative to the mineral-matter-free values, could be due to loss of B as BF_3 from the latter during acid digestion.

The ion exchange data on some elements, such as Ca in three different coals shown in figure 15, help explain most of the differences observed between extrapolated values (zero percent recovery) derived from washability data and mineral-matter-free values (acid extracted). Likewise magnesium is either soluble or undergoes exchange reactions. This is especially apparent in the western and low rank coals where more than 70 percent of the total concentrations of both Ca and Mg were removed. Sodium values indicate

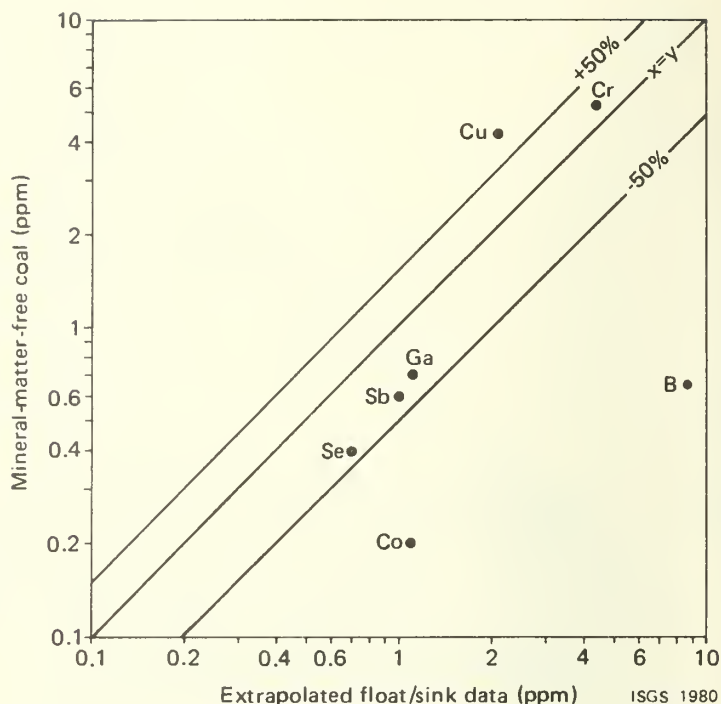


Figure 14. Comparison of independently determined concentrations of organically associated trace elements in the Herrin (No. 6) seam coal, Illinois (C16137).

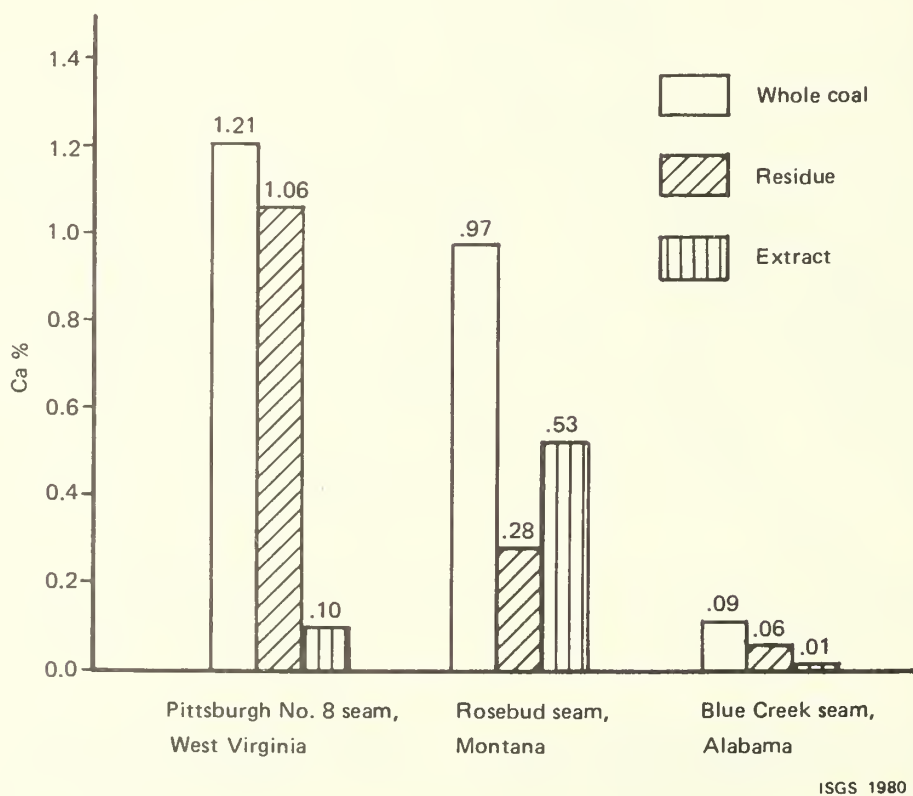


Figure 15. Elemental concentration of calcium in ammonium acetate (ion-exchanged) samples.

nearly total exchange or solubility in all cases but one. The exception is coal C-19824, which is unique in that 95 percent of the internal surface area consists of relatively small micropores less than 5 microns in size. It is suspected that pore size is a contributing factor in exchange or solubility reactions for both Na and Cl and probably for other elements as well.

The data in table 18 show that no significant quantity of Al, Si, P, S, K, Fe, V, Ti, Ni, Cu, Zn, As, Br, or Pb are attached to the coals in an exchangeable form or occur as a mineral that is soluble in the exchange medium used (ammonium acetate). Thus exchangeable ions, which are not removed during float-sink procedures, remain with the coal organic fraction and tend to increase organic affinities of these elements. The acid extraction procedure, however, removes the exchangeable and/or soluble ions attached to surfaces of the polymerized coal.

This evidence suggests that exchangeable ions may be contained in associated ground water after initial polymerization has taken place—perhaps even being a result of present-day conditions. The amount of surface area made available to exchange reactions through grinding of coal is a very small percentage of the actual surface area that would be present if the material were totally depolymerized. These data indicate that virtually all of the exchangeable elements can be removed by the acid treatment. It seems likely that adsorption occurs on the surfaces of the coal particles and pores.

The same logic applies to elements that may be chelated with organic material. If major portions of such elements can be removed, they probably come from the available surface area, and chelation probably occurred after the initial polymerization had taken place, and the coal structure had become at least partially fixed.

While some disagreement exists in the values derived from the two independent procedures for investigating elemental occurrence in coal, an accounting of these differences can be logically made. Moreover, agreement of trace element concentrations, determined in acid-extracted mineral-free coal and the concentrations calculated from adjusted washability curves, is sufficiently good to permit their use as estimates of absolute quantities of elements associated with coal organic material. These concentrations, for the most part, are relatively low.

VARIABILITY OF ORGANICALLY ASSOCIATED ELEMENTS

Table 6, which compares elemental concentrations of the raw coal and the the mineral-matter-free material, illustrates the large amount of variability among coals. For example, in two high-rank eastern coals, the retained cobalt is 72 percent in sample C-18820 but only 10 percent in C-19824. A different effect can be shown for titanium; a retention of about 200 ppm results in a percentage of 16.6 percent in C-18820, while a retention of only 39 ppm in C-18440 results in a slightly higher 19.5 percent of titanium remaining in the demineralized material. Therefore, knowledge of only the total concentration of an element in a coal without knowledge of its organic affinity is of little use in estimating the percentage associated with organic matter. Table 7 gives the mean retention percentages of each organically associated trace element for each of the geographical regions studied.

The degree to which coals in this study are representative members of their respective regions is illustrated in table 22. Predicted concentrations of an element in mineral-matter-free (demineralized) material were calculated by multiplying the mean values for each element in whole coal (given in Gluskoter et al. [1977], tables 8 through 10) by their respective mean retention factors found in this study (table 7). Agreement between the mean of predicted values and mean of determined values for the limited number of samples included (24) is generally very good. Poor agreement occurs particularly for elements where the uncertainty for retention values is greatest, i.e., at low concentrations.

Table 7 summarizes the mean elemental concentrations in coals for the three geographical regions. The table presents evidence that for some elements greater variations in concentrations occur *within* a geographical area than *between* such areas. Especially for whole coal, the standard deviations within a single seam can exceed the mean concentrations in some instances (see also Gluskoter et al., 1977, p. 121). For example, in the Herrin (No. 6) coal seam (see tables 1 and 6), both the inorganic and the organic components vary widely. Such differences demonstrate the need for each coal to be considered on an individual basis.

Perhaps a better overall perception of the variability of organically associated elements can be gained from the data in table 23. The total mean retention percentages for all elements are combined, and the summation of all element concentrations have been calculated for each demineralized coal (values do not include sulfur). No relationship was observed between data concerning ash content of the whole coals and other data in table 23. Despite the apparent consistency in total mean retention percentages, large standard deviations indicate wide concentration variations of the organically associated elements within regions. Further, correlations made between all pair combinations of organic affinities for Illinois No. 6 coal indicate that knowledge of the organic association of one element is of little value in predicting the organic association of other elements.

There is also an apparent lack of correlation between the residual trace element concentration and the internal surface area of coal (table 23, last column). If this characteristic of coal organic matter had significantly affected results of the demineralization procedure, i.e., influenced extraction of certain elements, correlation between surface area and the percentage of trace elements removed should have been observed. This evidence indicates that most organically associated elements are actually contained within the polymerized structure of the coal. Minerals and exchangeable ions or, perhaps, chelated elements on the surfaces of the coal particles are the materials thought to be removed by acid leaching.

COMPARATIVE DATA

Table 24 shows some of the relationships between the organically associated elements in coal and concentrations of the same elements in plant material. This table presents the overall mean concentrations of the organically associated elements from this study, mean plant values compiled by Siegel (1974), the mean crustal abundance of elements compiled by Mason (1958), and certified values for the orchard leaves samples of the National Bureau of Standards (SRM 1571). For the latter, additional values determined at the Illinois State Geological Survey have been added. A few mean values

TABLE 22. Prediction of mean elemental concentrations in mineral-matter-free coal for three basins.

Element	All values ppm unless noted					
	Illinois		Eastern		Western	
	Predicted mean* (114)	Actual mean† (15) (N)	Predicted mean (23)	Actual mean (6) (N)	Predicted mean (28)	Actual mean (6) (N)
Si	72	65	56	60	85	56
Al	72	74	170	144	100	76
Fe	100	76	150	106	106	71
Ca	67	50	70.5	71	170	61
Na	10	7.9(13)	16	10(5)	28	7.8
Mg	45	47(12)	42	25(3)	14	17(3)
K	17	11(9)	2.5	1.8(3)	3	<
Ti	24	31	72	76	45	31
P	5.8	4.3(14)	6	2.8(4)	3.9	2.5(2)
Mn	1.06	1	1.8	2.4(5)	1.96	1.8
S	1.6%	1.6%	1.2%	1%	0.45%	.42%
Organic S	1.6%	1.6%	0.86%	.98%	0.53%	.42%
Be	0.05	.05	0.09	.06	0.05	.03(5)
B	17	8	17	14	9	7
Sc	.49	.53	1.3	1.3	0.4	.3
V	4.5	5.5(13)	7	9.3	3	2.3(5)
Cr	4.5	6(14)	7	7	1.6	1
Co	.80	.45(14)	4	3.5	0.6	.5
Ni	6.1	5.1(7)	4	2.8(5)	<	<
Cu	3	4(12)	3	4	2	4
Zn	15	2.7(3)	<	<	<	<
Ga	1.9	0.6(14)	1.7	1.1	0.9	0.7
As	0.7	0.2(2)	1.7	.3(1)	0.9	.5(4)
Se	0.3	0.4(14)	0.9	0.6	0.4	0.4
Br	8.5	7.7	9	9.7	3.6	1.7
Rb	1.1	3(1)	<	<	<	<
Sr	5.6	5.7(9)	27	29(3)	8	4(2)
Mo	.65	.87(4)	<	<	0.4	1.4(1)
Cd	.37	.67(4)	<	<	<	<
Sb	.44	.38(12)	0.4	.4	0.3	.38
Cs	.08	.06(8)	0.1	.08(4)	0.07	.01(1)
Ba	6	3.3(11)	28	20	15	13
La	0.9	0.9	3.7	2.7	1.1	1.3
Ce	1.4	1.5	4.2	3.2	1.9	1.7
Sm	.4	.3	.73	.54	0.2	.21
Eu	.05	.06	.19	.12	0.06	.05
Tb	.06	.09(6)	.10	.04(1)	0.08	.05(2)
Dy	.34	.28(10)	.94	.66(3)	0.22	.19(2)
Yb	0.14	0.14	0.36	0.23	0.11	0.1
Lu	.02	.03(12)	.08	.06(5)	0.02	.02(5)
Hf	.08	.11(13)	0.29	.29	0.21	.26
Ta	.04	.05(5)	0.10	.09(3)	0.08	.09(2)
W	.21	.38(7)	0.20	.26(4)	0.16	.22(2)
Pb		<	---	<	---	<
Th	.52	.55	1.2	2.6	0.76	.8(5)
U	.28	.22(10)	0.3	.27(4)	0.20	.13(5)

*Mean percentage retention (table 7) times mean elemental concentration (Gluskoter et al., 1977).

†Mean elemental concentration determined (table 7).

TABLE 23. Total retention percentages of elements and concentration summations for demineralized coal and ash or mineral-matter content for whole coal

Coal sample	Total mean retention* (%)	Number of elements for mean†	Sum. of elements determined (ppm)	High-temp. ash (%)	Low-temp. ash (%)	Surface area CO ₂ (m ² /g)
EASTERN						
C 18820	22±21	33	735	11.5	12.9	327
C 18841	17±15	29	980	10.2	14.5	53
C 18848	20±20	26	514	11.6	12.7	98
C 18844	22±19	26	510	8.3	10.4	56
C 19824	26±31	33	296	11.0	14.5	68
C 18824	20±16	30	418	12.5	14.7	112
Mean			575.5±245	10.8±1.4	13.3±1.7	
WESTERN						
C 18816	16±20	28	273	9.0	10.6	277
C 19000	21±17	24	756	7.0	8.7	240
C 19854	30±36	30	191	11.6	13.1	236
C 18440	19±19	28	305	9.8	14.7	147
C 18445	19±21	26	272	7.5	10.2	232
C 18457	21±19	29	294	6.3	8.2	219
Mean			348.5±204	8.5±2	10.9±2.5	
ILLINOIS						
C 14684	17±15	33	448	9.9	12.3	163
C 15999	17±15	34	415	12.4	15.1	155
C 16543	12±14	34	332	11.9	16.2	254
C 16993	14±20	31	415	16.0	20.6	87
C 17001	21±24	28	681	11.8	16.0	97
C 18126	11±11	33	277			209
C 16317	18±18	29	340			215
C 18304	14±12	31	719	10.9	14.5	85
C 18320	17±17	31	309	13.8	16.8	79
C 18368	15±21	31	265	13.2	16.4	80
C 18560	14±20	31	253	16.5	20.4	79
C 18571	14±15	25	377	16.9	23.4	241
C 18704	12±13	31	423	17.1	21.7	218
C 18748	16±17	33	287			35
C 18857	14±12	26	264	13.9	17.4	227
Mean			387±143	13.7±2.4	17.6±3.3	

*Except sulfur.

†Number of elements used to determine the mean. "Less than" values not included.

for peat taken from Casagrande (1976) are included to illustrate concentrations of certain elements in a modern coal-forming type of environment.

The only elements in coal that show concentrations significantly in excess of crustal abundance (clark values) are S and Se (Gluskoter et al., 1977). This is expected because the chemistry of these elements is very similar. They occur at concentrations of 50 to 20 times the clarke value. Most of the elements that are found in relatively high concentrations in plants (Fe, Ca, K, Mg, Na, P) and certain of the other known nutrients such as Mn, B, and Zn are less concentrated in the organic fraction of coal than in plant material. Perhaps these elements are in soluble or mobile forms that are readily leached from the material during epigenesis before polymerization takes place. Conceivably, some may also have been leached from the coal by the acid extraction, as in the case of the exchangeable ions studied.

TABLE 24. Mean MMF values for coal compared to plant material and crustal abundance (ppm)

Element	Mean MMF	Mean (plant)*	NBS [†] (orchard leaves)	Crustal [‡] abundance	Peat**
Si	59	200-5,000	480	277,200	
Al	63	0.5-4,000	400	81,300	
Fe	60	140	290	50,000	339 (25-2,100)
Ca	39	18,000	20,900	36,300	5,396
Na	3.1	1,200	78	28,000	3,580 (77-20,700)
Mg	16	3,200	6,000	20,000	965 (200-4,750)
K	3.9	14,000	14,000	25,900	6,525 (4-35,000)
Ti	34	1	0.06	4,400	
P	3.1	2,100	2,300	1,050	
Mn	1.0	630	0.91	950	121 (7-701)
S	12,200	3,400	1,900	260	
Be	0.05	<.1	0.03	2.8	
B	10	50	33	10	
Sc	0.7	0.008		22	
V	4.8	1.6	0.7	135	
Cr	5.9	0.23	2.3	100	
Co	1.2	0.5	0.2	25	
Ni	3.4	0.3	1.3	75	
Cu	2.5	14	12	55	
Zn	0.7	100	25	70	
Ga	0.6	0.06	0.08	15	
As	0.15	0.2	10	1.8	
Se	0.4	0.2	0.08	0.05	
Br	4.4	15	10	2.5	
Rb	0.25	20	12	90	
Sr	5.9	26	37	3.75	
Mo	0.3	0.9	0.3	1.5	
Cd	0.1	0.6	0.11	0.2	
Sb	0.3	0.06	3.0	0.2	
Cs	0.06	0.2	0.04	3	
Ba	6.5	14	51	425	
La	1.4		0.09	30	
Ce	1.3		1	60	
Sm	0.3	0.006		6.0	
Eu	0.08	0.03	0.3	1.2	
Tb	0.09	0.002		0.9	
Dy	0.6	0.02		3.0	
Yb	0.18	<0.02	3.3	3.4	
Lu	0.05			0.5	
Hf	0.17	0.01		3	
Ta	0.04			2	
W	0.18	0.07	<2	1.5	
Pb	0.2	2.7	45	13	
Th	0.5		65	7.2	
U	0.2	0.04	0.03	1.8	

*Siegel, 1974. Values on dry weight basis.

†Various literature sources. Values on dry weight basis.

‡Mason, 1958.

**Casagrande, 1976. Values on dry weight basis.

From the coal washability and demineralization data it seems probable that the largest portion of trace and minor elements are not associated with the organic fraction of the coal.

IMPORTANCE OF MINERAL MATTER

Although many elements exhibit some organic association, the total elemental content of acid-demineralized coals in tables 9 through 17 generally is low, ranging only from 250 to 600 ppm (excluding organic sulfur). Addition of exchangeable, soluble, and chelated elements still results in the conclusion that most of the trace and minor elements in coal are in a mineral form and are subject to significant reduction by physical cleaning procedures.

Sulfides, sulfates, carbonates, quartz, and clay minerals, together with small amounts of many other minerals, form a multi-component system in the coal with complex origins and variable chemical compositions. The chemical elements present in the mineral matter occur not only as major components of minerals but also, to a limited extent, as isomorphic replacements in solution or as exchangeable cations on clays. These types of sites in the mineral matter are presumably the position of many of the trace elements found in coals.

Table 25 gives the principal minerals commonly found in coals and some of the trace elements associated with them. These associations have been compiled from the results of trace element investigations of coal (Gluskoter et al., 1977; O'Gorman and Walker, 1972; Miller and Given, 1978) and from reviews of basic geochemical and mineral research (Deere et al., 1966; Weaver and Pollard, 1973; and Grim, 1968).

Kaolinite, illite, and expandable clays commonly make up a major portion of the mineral matter of most coals. Cation adsorption and exchange are important properties of these minerals. The minor and trace alkali and alkaline earth elements are favored for the exchangeable sites in clays. Because of inherent higher cation-exchange capacities, illites, montmorillonites, and mixed-layered clays tend to adsorb a greater variety of ions than kaolinite. A number of elements are also known to substitute for Al, Si, and other major constituents bound into the crystal lattice. Determinations of trace elements in partings and shale strata associated with coal seams indicate higher concentrations of many minor and trace elements in these components, but because of the complex combinations of clays and other incorporated minerals, specific mineral-trace element associations are inconclusive.

COAL CLEANING APPLICATION

Knowledge of the distribution and form of elements within a coal will allow better predictions of the cleaning potential for coal than are now possible. Table 26 shows the wide differences in the organic association of trace elements in coals; broadly speaking these differences may be classified within each of the three major coal-producing areas.

For the Illinois coals used in this study, Br, Ge, Be, Sb, B, and organic sulfur consistently fall in the organic phase. The sulfide-forming elements, Zn, As, Cd, Fe, and pyritic sulfur, are consistently found in the most inorganic fraction and can, therefore, usually be materially reduced by gravity

TABLE 25. Elements commonly associated with the principal minerals found in coals*

Mineral phases	Major constituents	Trace constituents
Sulfides		
Pyrite, marcasite	Fe, S	{ As, Cd, Hg, Ag, Pb, Fe, Zn, Cu, Co, Sn, Ni, Mo, Se, Ga
Sphalerite	Zn, S	
Galena	Pb, S	
Sulfates		
Barite	Ba, S	Sr, Pb, Ca
Gypsum	Ca, S	
Carbonates		
Calcite	Ca	{ Ba, Sr, Pb, Mn, Ca Fe, Mg
Siderite	Fe	
Ankerite	Ca, Fe	
Dolomite	Ca, Mg	
Phosphates		
Apatite	Ca, P, F	Rare earths, U, Ce, Mn, Cl, Mg
Silicates		
Quartz	Si	Hf, Th, P Li, F Ba, Sr, Mn, Ti, Fe, Mg Rb, Ba, Sr, Fe, Mg, Ti, Li F, Rb, Cs, Ba, Mg, Fe
Zircon	Si, Zr	
Tourmaline	Ca, Mg, Fe, B, Al, Si	
Plagioclase feldspar	Ca, Na, Al, Si	
Apali feldspar	K, Al, Si	
Muscovite	K, Al, Si	
Clay minerals		
Kaolinite	Al, Si	Ti, Mg, Fe, and others
Illite	Al, Si, K	{ Fe, Mg, Ca, Na, K, Ti, Li, V, B, Mn, Cr, Cu, Ni, Rb, Cs, Ga, Be, Zn, Se, F, La, Ba, Sr, Co, and others
Montmorillonite	Al, Si, Mg, Fe	
Mixed layer clays	Al, Si, K, Mg, Fe	
Chlorite	Al, Si, Fe, Mn, Mg	

*This partial listing does not preclude the probability of additional mineral-trace element associations.

separation procedures. A number of other elements, Zr, Hg, Pb, Hf, and Mn, also are highly inorganic in association and can be removed rather easily. The other elements determined—Al, Si, Ti, Mo, K, P, Ga, Ca, Cr, Co, Ni, Cu, Mg, Se—are either intermediate in their association or highly variable.

Br, Ge, Sr, and organic sulfur have some of the highest organic affinities and As, Rb, K, and pyritic sulfur are among the highest inorganic affinities in the eastern United States coals. Other elements that show relatively high organic associations are B, Ba, Be, Br, and Co. The remaining elements are variable or intermediate in their association.

The western coals contain a larger number of elements with high organic affinities (B, Mg, Br, Sr, Be, P, Na, and Ca) than coals studied from either of the other regions. Elements such as Si, As, Cs, Hg, Pb, and pyritic sulfur are highly inorganic; the other elements are variable in their associations.

In a physical cleaning process the elements that have high organic affinities are difficult to remove; conversely the inorganic elements are

TABLE 26. Organic association of trace elements in coal: Illinois coals

C18560	C17001	C18126
Herrin (No. 6) Coal Member Illinois	Davis Coal Member Illinois	Herrin (No. 6) Coal Member Illinois
Float-sink set No. 1	Float-sink set No. 2	Float-sink set No. 3
Ge 1.76	Ge 1.28	Ge 1.29
U	ORS	ORS
ORS	B	B
Hg	Be	Be
V	Ni	Sb .67
Br	Na, Ti	
Sb	P	
Dy	Cr, Se	
Be .87	Sb	
	Ga .66	
B, Cr .77	Co .65	SUS .62
Ni	Ca, K	V
Co	V	TOS
Eu	Al	Mo
Cu	Cu .56	Na
Na		Ga .40
Lu		
Sc		
K		
Th		
Ag		
Yb .52		
Zr .49	Si .50	Se .39
Hf	Mg	Cr
TOS, Rb, Ti	Mn .35	Ni
Cs, Ta		Co
Sm		Hg
Pb		Cu .25
Al		
Si		
Se		
Mg .27		
SUS .17	Zr .23	P, Fe, Ti .16
Sn, HTA, LTA	HTA	Zr, K
Ba, Ga	LTA	LTA, PYS
Cd, Ce, Sr	TOS	Al, HTA
Mn, Ca, Fe	As, Hg	Si
PYS	Mo, Pb, Fe	As, Pb
As, La, Zn	Cd, PYS	Cd, Mn, Zn, Ca .04
P .03	Zn, SUS .02	

TABLE 26. *Continued.* Eastern coals

C18841	C19824	C18820	C18848
Pittsburgh No. 8 Seam West Virginia	Pittsburgh No. 8 Seam West Virginia	Pocohontas No. 4 West Virginia	Blue Creek Alabama
Float-sink set No. 4	Float-sink set No. 5	Float-sink set No. 6	Float-sink set No. 7
ORS 1.07	ORS 1.15	ORS 1.18	Br 1.20
Sr	B	Co	Ge
Br	Br	Sn	Co
B	Sr	Br	ORS, TOS
U	Ba	Ni	SUS
Ba	TOS	Sr	Hg
P, TOS	Co, Ga	Be	Ni 1.01
Ge .69	Be	W	
	U, Yb	Ba	
	Sm	Ge	
	Na .71	Fe .67	
Cd .66	Ce, La, P .68	P .65	Sr .80
Dy	Dy, Eu, I, Sc, W	Dy, Yb	Cu, Dy
Pb	Li	Eu	Be
Eu, Na	Lu, Ni, Th, Al	V	V
Be, Co, Ga .53	Cr, Ti	Cu, Sb	La
	V	Tb	Ag
	Se	Ca	U
	Ta .51	Ag, Lu, Zn .52	W
			Lu
			Pb, Sn
			Sm, Tb
			Eu, Ga, Sb, Ce
			PYS
			Ba
			Cr, P, Zr
			Se
			Yb
			Ti
			Sc .53
Ca .50	Cu .49	Na .50	Cd .45
Mg	Hg	Ga	Hf, Fe
V	Hf	B	Th
Cu	Si	Se, Sm	Al
Hg	Sb	La	B
La	Zn	Mn, U	Ta, Ca .34
Ni, Sm	Cs	Cr, Pb	
Mn	Zr .27	Mg	
Zn		Th, Ti	
Ce, Sb		Hg, Ta .28	
Cr, Sc			
Se			
Sn			
Al			
Tb			
Yb			
Zr, Fe, Hf .30			
Lu .26	Rb, PYS .18	Hf .24	Zn .21
As, PYS	Fe	Zr	Na
Ta	HTA	Cs	LTA
Th	LTA	Rb, K	HTA, Si
Rb	SUS	Si	K
LTA	As	PYS	Cs, Rb
SUS	K	As .07	Mg
HTA	Cd		As, Mn .05
K, Si	Sn		
Cs	Mn, Tl		
Ti .05	Mo, Pb, Ca, Mg .04		

TABLE 26. *Continued.* Western coals

C19854		C19000	
Rosebud Seam Montana		Black Mesa Field Arizona	
Float-sink set No. 8		Float-sink set No. 9	
B	1.24	Zn	2.2
W		B	
ORS		Na	
P		Cd	
Br		Mg, ORS	
Sr		P	
Mg		Ba	
Sb		Fe	
La		Ni, TOS	
Ce, Eu		Sr	
Na		Br, Co	
Mo		Dy, Ca	
Ca		Ag	
Co		Be	.79
Tb			
Sc			
Dy			
F, Ga			
Ge, Yb			
Be, Sm	.73		
Lu	.68	Yb	.75
Al		V, Cu	
Ni		Lu	
Ta		Sb	
V		Ce, Sc	
U		Se	
Th	.56	La	
		Eu	.57
Cu	.44	Cr, Tb	.54
Hf		Mn, K	
Ag	.33	W	
		U	
		Hf, Sm	
		Zr	
		Rb	
		Ta, Al	
		Ga, Th	
		Ti	
		Sn	.29
Ti	.15	HTA	.22
Li		Hg	
LTA		LTA	
Tl		PYS	
Cr		As	
HTA		Si	
Cd, Si		Pb	
Se		Cs, Ge	.03
Mn, Pb, Sn, Zr			
As, Cs, Hg, Rb			
PYS, Ba, I, Zn, Fe, K, SUS, Tos	.02		

more easily removed. Depending on the coal, the elements that are intermediate or variable in their association will exhibit a limited potential for reduction or a large variation in procedures for removal. The low-rank western coals contained the largest number of elements not readily removed by standard washing methods (table 26), in many cases, these elements have rather low concentrations and would not be expected to present a problem.

The potential for reduction of elements and minerals in coal, however, is dependent on characteristics other than just their organic-inorganic associations. The particle size of the minerals plays a significant role in the reduction potential. For example, 95 percent of the pyrite occurring in coal C-19824 has an average particle size of only 8 microns, and 15 percent of the pyrite is encapsulated within the coal particles; this makes its removal extremely difficult. (Kuhn et al., 1978). (For all practical purposes, such particles are "organically associated.") Furthermore, if an element such as Mn is associated with calcite, its removal is easier than if associated only with clay minerals. Clays tend to concentrate in the lighter fractions of the coal, and they are often finely dispersed within the macerals. Compositional trends of the two coals selected for clay analysis (table 21) show higher proportions of kaolinite in the lighter fractions and increased amounts of illite and mixed-layer clays in the 1.60 S fractions.

Such variations have a practical importance for utilization. The composition of the clay and other minerals in coals affects the fusion temperature of the resulting ash. White and O'Brien (1964) have indicated that increased concentrations of illite, especially in conjunction with higher amounts of carbonate, will lower the melting point and viscosity and change the glass-forming characteristics of the ash. (See also Kent and Champion, 1964) If a portion of the clays is removed during cleaning, the resultant clay composition may substantially change; trace element contents and adsorption properties are altered as well as fusion and sintering characteristics of the ash.

These considerations and others, such as variability among and within coal seams, will modify interpretations placed upon organic affinities or associations. The organic affinity index when it is used in conjunction with these factors will be most useful in quantifying the potential for coal cleaning.

REFERENCES

- American Society for Testing and Materials, 1978a, Preparing coal samples for analysis, D 2013-72, *in* 1978a Annual Book of ASTM Standards, Part 26: Gaseous Fuels; Coal and Coke; Atmospheric Analysis: ASTM, Philadelphia, p. 279-293.
- American Society for Testing and Materials, 1978b, Test for forms of sulfur in coal, D 2492-77, *in* 1978 Annual Book of ASTM Standards, Part 26: Gaseous Fuels; Coal and Coke; Atmospheric Analysis, ASTM, Philadelphia, p. 332-337.
- Bishop, M., and D. L. Ward, 1958, The direct determination of mineral matter in coal: *Fuel*, v. 37, p. 191-200.
- Casagrande, D. J., and L. D. Erchull, 1976, Metals in Okefenokee peat-forming environments: relation to constituents found in coal: *Geochim. et Cosmochim. Acta*, v. 40, p. 387-393.
- Cavallaro, J. A., A. W. Deurbrock, H. Schultz, G. A. Gibbon, E. A. Hattman, 1978, A washability and analytical evaluation of potential pollution from trace elements in coal, EPA-600/7-78-038, March.
- Deere, W. A., R. A. Howie, J. Zussman, 1966, An introduction to the rock forming minerals: Longmans, Green and Co., LTD, London, 528 p.
- Fiene, F. L., J. Kuhn, H. J. Gluskoter, 1978, Mineralogic affinities of trace elements in coal: Presented at EPA Symposium on Coal Cleaning to Achieve Energy and Environmental Goals, Hollywood, Florida, Sept. 11-15.
- Gluskoter, H. J., 1965, Electric low-temperature ashing of bituminous coal: *Fuel*, v. 44, p. 285-291.
- Gluskoter, H. J., 1975, Mineral matter and trace elements in coal, *in* S. P. Babu [editor], Trace elements in fuel: American Chemical Society, Washington, D. C., Advances in Chemistry Series No. 141, p. 1-22.
- Gluskoter, H. J., R. R. Ruch, W. G. Miller, R. A. Cahill, G. B. Dreher, and J. K. Kuhn, 1977, Trace elements in coal: occurrence and distribution: Illinois State Geological Survey Circular 499, 154 p.
- Goldschmidt, V. M., 1935, Rare elements in coal ashes: *Industrial and Engineering Chemistry*, v. 27, no. 9, p. 1100-1102.

- Grim, R. A., 1968, Clay mineralogy: McGraw-Hill, New York, 596 p.
- Helfinstine, R. J., N. F. Shimp, J. A. Simon, and M. E. Hopkins, 1971, Sulfur reduction of Illinois coals—washability studies. Part 1: Illinois State Geological Survey Circular 462, 44 p.
- Helfinstine, R. J., N. F. Shimp, M. E. Hopkins, and J. A. Simon, 1974, Sulfur reduction of Illinois coals—washability studies. Part 2: Illinois State Geological Survey Circular 484, 32 p.
- Helfinstine, R. J., J. A. Simon, N. F. Shimp, and M. E. Hopkins, 1970, Sulfur reduction of Illinois coals—washability tests: Illinois State Geological Survey Environmental Geology Note 34, 12 p.
- Holmes, J. A., 1911, The sampling of coal in the mine: U.S. Bureau Mines Technical Paper 1, 18 p.
- Horton, L., and K. V. Aubrey, 1950, The distribution of minor elements in vitrain: three vitrains from the Barnsley seam: Journal of the Society of Chemical Industry, London, v. 69, suppl. no. 1, p. S41-S48, (revised).
- International Organization for Standardization, 1974, Determination of mineral matter in coals: ISO 602, available from American National Standards Institute, NY.
- Kent, C. R., and A. O. Champion, 1964, The influence of carbonate minerals in the ash-fusion characteristics of coals; *in* Symposium on the inorganic constituents of fuel (origin, influence and control): University of Melbourne, May 21-22, p. 83-100.
- Kuhn, J. K., F. L. Fiene, and R. D. Harvey, 1978, Geochemical evaluation and characterization of Pittsburgh No. 8 and a Rosebud seam coal. U. S. Department of Energy, Morgantown Energy Technology Center, Morgantown, WV, METC/CR-78/8, 53 p. (Available NTIS)
- Kuhn, J. K., D. Kidd, J. Thomas, Jr., R. Cahill, D. Dickerson, R. Shiley, C. Kruse, and N. F. Shimp, 1978, Volatility of coal and its by-products *in* Symposium Proceedings: Environmental aspects of fuel conversion technology, III (Sept. 1977, Hollywood, FL): EPA-600/7-78-063 April, p. 431-446.
- Kuhn, J. K., L. B. Kohlenberger, and N. F. Shimp, 1973, Comparison of oxidation and reduction methods in the determination of forms of sulfur in coal: Illinois Geological Survey Environmental Geology Note 66, 11 p.
- Lawlor, D. L., J. I. Fester, and W. E. Robinson, 1963, Pyrite removal from oil-shale concentrates using lithium aluminum hydride: Fuel, v. 42, no. 3, p. 239-244.
- Majahan, O. M., and P. L. Walker, Jr., 1979, Effect of inorganic matter removal from coals and chars on their surface areas: Fuel, v. 58, p. 333-337.

- Mason, B., 1958, Principles of Geochemistry: Wiley, New York, 2nd ed., 310 p.
- Miller, R. N., and P. H. Given, 1978, A geochemical study of the inorganic constituents in some low rank coals. Technical Report, Pennsylvania State University; Report FE-2494-TR-1 submitted to U.S. Dept. of Energy under contract No. EX-76-C-01-2494, 314 p.
- Nicholls, G. C., 1968, The geochemistry of coal-bearing strata, *in* D. Murchison and T. S. Westoll [editors], Coal and coal-bearing strata: American edition, American Elsevier, New York, p. 269-307.
- O'Gorman, J. V., and P. L. Walker, Jr., 1972. Mineral matter and trace elements in U.S. coals: Office of Coal Research, U.S. Department of the Interior, Research and Development Report No. 61, Interior Report No. 2, 184 p.
- Rao, C. P., and H. J. Gluskoter, 1973, Occurrence and distribution of minerals in Illinois coals: Illinois State Geological Survey Circular 476, 56 p.
- Ruch, R. R., H. J. Gluskoter, and N. F. Shimp, 1974, Occurrence and distribution of potentially volatile trace elements in coal: A final report: Illinois State Geological Survey Environmental Geology Note 72, 96 p.
- Russell, S. J., and S. M. Rimmer, 1979, Analysis of mineral matter in coal, coal gasification ash, and liquefaction residues by scanning electron microscopy and x-ray diffraction, *in* C. Karr [editor], Analytical methods for coal and coal products; v. III, chapter 42, p 133-162.
- Siegel, F. R., 1974, *Applied Geochemistry*: Wiley-Interscience, New York, 353 p. (p. 139-142).
- Stepusin, S.M.R., 1978, Vertical variations in the mineralogical and chemical composition of the underclay of the Herrin (No. 6) Coal in southwestern Illinois: MS thesis, University of Illinois, Urbana, 68 p.
- Ward, C., 1977, Mineral matter in the Springfield-Harrisburg (No. 5) Coal Member in the Illinois Basin, Illinois State Geological Survey Circular 498, 35 p.
- Weaver, C. E., and L. D. Pollard, 1973, The chemistry of clay minerals: Elsevier Scientific Publishing Co., Amsterdam, London, New York, 213 p.
- White, W. A., and N. R. O'Brien, 1964, Illinois clay resources for lightweight ceramic block: Illinois State Geological Survey Circular 371, 15 p.
- Yancey, H. F., and M. R. Geer, 1962, Behavior of clays associated with low-rank coals in coal-cleaning processes; Bureau of Mines Report of Investigations 5961, 10 p.

- Zubovic, Peter, 1960, Minor element content of coal from Illinois beds 5 and 6 and their correlatives in Indiana and western Kentucky: U.S. Geological Survey, open file report, 79 p.
- Zubovic, Peter, 1966, Physiochemical properties of certain minor elements as controlling factors of their distribution in coal, *in* R. F. Gould [editor], Coal science: Washington, D.C., American Chemical Society Publications, Advance in Chemistry Series, no. 55, p. 221-246.
- Zubovic, Peter, 1976, Geochemistry of trace elements in coal, *in* F. A. Ayer [compiler], Symposium proceedings: Environmental aspects of fuel conversion technology, II: (December 1975), Washington, D.C., U.S. Environmental Protection Agency, Environmental Protection Technology Series EPA-600/2-76-149, p. 47-63.
- Zubovic, P., T. Stadnichenko, and N. B. Sheffey, 1960, The association of minor elements with organic and inorganic phases of coal: U.S. Geological Survey Professional Paper 400-B, p. B84-B87.
- Zubovic, P., T. Stadnichenko, and N. B. Sheffey, 1961, The association of minor element associations in coal and other carbonaceous sediments: U.S. Geological Survey Professional Paper 424-D, Article 411, p. D345-D348.
- Zubovic, P., T. Stadnichenko, and N. B. Sheffey, 1964, Distribution of minor elements in coal beds of the Eastern Interior region: U.S. Geological Survey Bulletin 1117-B, 41 p.

